



UNITS 13–14 CHEMICAL REACTIONS AND THE PERIODIC TABLE

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STUDY GUIDE

These two Units have several components: the text, five experiments, an exercise with cards, and two TV programmes. The emphasis is on certain deductions that bring order to the behaviour of the chemical elements. These deductions are based on experimental studies of chemical composition and chemical properties, which is why you will be doing several experiments. This aspect of your work may well determine your study plans.

First you should organize your work into sessions that will enable you to complete the experiments, some of which are assessed in assignments. These experiments are listed below, together with typical completion times, which include the time you will require to clear up and pack away the apparatus. The times are for guidance; if you have some experience of practical work, you may find you will complete the experiments more quickly. If you are inexperienced, you may take longer.

Experiment 1	: 40 minutes
Experiment 2	: 3 hours
Experiment 3	: 30 minutes
Experiment 4	: 45 minutes
Experiment 5	: 40 minutes

You may find it most convenient to perform the experiments as you come to them, or to do the experiments in three sessions as we suggest (Experiments 1 and 3; Experiment 2; and Experiments 4 and 5), or to do all of the experiments in a single session. This will obviously save time in setting up and clearing away.

Next you will need to find a place to work. You need a flat bench surface about a metre wide. You should cover your work surface with the bench-cote provided to protect it from any substances that you spill on it. The solution of iodine in Experiment 2 will cause stains, although these can be removed with a solution of sodium thiosulphate, which you can obtain from a chemist's shop. It should be possible to ventilate the room in which you work although you will also need a draught-free area in which to use the balance. This problem may be solved simply by opening and closing windows as appropriate.

Wherever you work be sure to follow this advice on safety.

Keep children and pets away from your experiments.

Do not perform the experiments next to food. (There is nothing particularly toxic in the Experiment Kit, but it is best to regard all chemicals as hazardous.)

Wear safety goggles (or your own spectacles) when doing the experiments.

Do not perform experiments near flames unless instructed to do so; some of the liquids are flammable.

Always follow the safety instructions in the *Experiment Kit booklet 2* before you carry out any experiments and if you have any mishaps.

When you have finished your experiments you will need to dispose of the chemicals. Follow the instructions given in the *Experiment Kit booklet 2* under 'Disposal of chemical residues'. Separate instructions are given for the disposal of the chemical residues from each experiment.

During your experiments you will need to record observations and data. Do this *directly* into your Notebook. Do not record your observations on loose pieces of paper because these are easily lost.

You will also need some extra items to do the experiments. Be sure to get these before you begin. The full list is given overleaf. Unless you have already done so, you should obtain as soon as possible the gas cylinder specified in the *Introduction and Guide*.

CHEMICAL FORMULA

CHEMICAL COMPOUND

adhesive tape
 battery, 9 volts (for example, a PP7)
 distilled water (about 1 litre)
 gas cylinder (PRIMUS 2202 butane cylinder with self-sealing safety valve)
 household rubber gloves
 kettle
 knife (domestic, kitchen)
 matches
 paper tissues
 sandpaper or emery paper
 scissors
 sheets of clean paper (two)
 small screwdriver
 white sugar

Besides these experiments, there is also an exercise with a set of cards that was mailed with these Units. The exercise is performed at intervals during your reading of Section 4, and at the end of each stage the cards should be left undisturbed in readiness for the next.

The first TV programme 'Elements discovered' is concerned with the discovery of the chemical elements, and can be viewed conveniently at any time in your study of these Units. Before viewing the second programme, 'Elements organized—the Periodic Table', you should have read at least as far as the end of Section 4.

In addition to the usual ITQs and SAQs, these Units contain 21 revision SAQs (numbers 37 to 57). These are *not* part of the two weeks' work allocated to these Units: they are there to help you later when you are revising.

I INTRODUCTION

These two Units introduce you to the fundamentals of chemistry. Chemists view the world as a collection of substances that are formed from the chemical elements. Therefore you will begin by making and examining some chemical substances. You will, for example, make a substance (or compound) from the elements tin and iodine, and you will actually be able to measure the ratio of the numbers of tin and iodine atoms that combine to form the compound.

Ratios of this kind enable us to represent chemical compounds using chemical symbols, and these representations are called **chemical formulae**. Chemical changes, in which one substance is transformed into others, are similarly represented by formulae. These formulae are therefore the language of chemistry.

By examining patterns that occur in these formulae we follow the reasoning of the great Russian chemist, Dmitri Mendeléev. He was able to arrange the elements in a tabular form according to the formulae of their compounds. His Periodic Table of the elements is generally agreed to be one of the greatest achievements in chemistry. Some rearrangement of Mendeléev's Table leads us to a revised Table that reflects the electronic configurations of the elements. Thus the formulae of compounds are related to the electronic configurations of the elements that they contain. We explore this relationship by examining how chemists describe the binding between atoms in chemical compounds.

Your studies will be based on your own observations in experiments done with your Experiment Kit. Therefore it is important that you plan and prepare for these experiments. The Study Guide contains advice on how to do this, as well as a list of items that you will need to obtain before you do the experiments. Read it now, if you have not already done so.

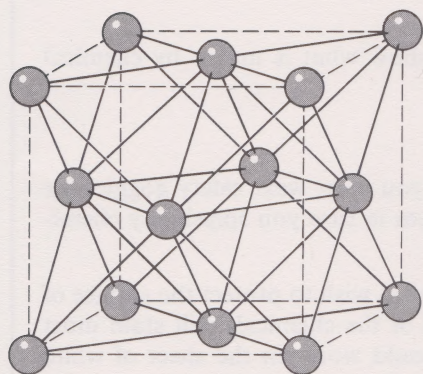


FIGURE 1 The arrangement of atoms in metallic copper. The lines shown joining the atoms are merely indicating their relative positions.

2 ELEMENTS, COMPOUNDS AND CHEMICAL REACTIONS

You have only to look around you to realize that the world consists of a variety of materials—rocks, air, metals, plastics, the contents of living organisms, water and the many substances dissolved in it, and so on. Yet this vast number of different substances is derived from fewer than ninety stable elements. This Section introduces some relationships between elements and the compounds that they can produce.

How would you define an element?

An element consists of atoms, all of which contain the same number of protons in their nuclei. This number is the atomic number Z . In an electrically neutral atom, the nucleus is surrounded by a number of electrons, equal to the number of protons in the nucleus. Copper is an element that you will make some use of in these Units. At the atomic level, copper is pictured as in Figure 1, which shows a small part of a crystal of copper. It contains only one kind of atom, and each of these atoms is surrounded by similar atoms in a regular array.

The formation of more complex substances from elements is familiar to you. Anyone who has a bicycle or car knows that if iron is left exposed to a wet atmosphere, it rusts. Rust is a red powder quite unlike shiny metallic iron, although rust does contain iron. If you are interested in preserving your car or bicycle, you are careful to keep the iron protected from the atmosphere, usually by a layer of paint. This vulnerability to rusting in the atmosphere suggests that there is something in the atmosphere that attacks metallic iron. One of the components of the atmosphere is the element oxygen (symbol O). In fact, rust consists of the two elements iron and oxygen, although it is plainly not merely a mixture of the shiny metal iron and the colourless gas, oxygen. In rust, these two elements are *combined* to form a new substance. Substances that consist of elements that are combined in this way are called **chemical compounds**, or often just *compounds* for short.

We must be careful to distinguish between materials that are *compounds* and materials that are *mixtures*. If you mix some sugar and sand together, it is obvious that you still have a mixture of sugar and sand: some of the grains are sugar and some are sand. Even if the sand and sugar are ground so finely that you cannot distinguish individual grains, it is still easy to separate the components of this mixture by pouring hot water onto it. This dissolves the sugar and leaves the sand behind. Sugar dissolves in hot water and sand does not, so the individual particles in the mixture still have the properties of sand and sugar.

This provides us with a crude *operational* definition of the distinction between a compound and a mixture, that is, a definition based on observable properties. Compounds are generally quite different in appearance and properties from the mixture of elements from which they are formed.

Can you think of any examples in which metals in common use form compounds?

You have probably noticed that copper roofs on civic buildings acquire a green coating; this is because the copper combines with gases in the atmosphere. Similarly, silver spoons do not stay shiny, especially if used for eating eggs. The black coating that develops over them is a compound of silver and sulphur, which is present in eggs.

To investigate more about the changes that occur when elements form compounds, you should now do Experiment 1. You may also find it convenient to do Experiment 3 now as the two experiments use the same pieces of apparatus. If you do Experiment 3 now, record the results in your Notebook—you will need them later.

EXPERIMENT I SOME REACTIONS OF COPPER COMPOUNDS

TIME

about 40 minutes

NON-KIT ITEMS

adhesive tape
gas cylinder
matches
Notebook
piece of paper (about 10 cm × 10 cm)

KIT ITEMS

Chemical tray
copper powder
dilute hydrochloric acid (2.4 mol l^{-1})
wire nail
zinc wool

Tray A
porcelain crucible

Tray B
beaker, 100 cm^3
boiling tubes (two)
evaporating basin
filter funnel

Tray C
Benchcote paper
crucible tongs
filter paper
measuring spoon (spatula-type)
nozzle for gas burner
pipeclay triangle
safety goggles
spatula
test-tube tongs
test-tube rack
tripod

AIM

The purpose of this experiment is to show what is meant by chemical reaction.

GENERAL NOTES

In all of the experiments in the Units, you must wear safety goggles (or your own spectacles) to protect your eyes in case you splash any chemicals.

In this and other experiments you may also wish to protect the surface of your workspace from chemicals. Some of the chemicals will stain most surfaces if spilled on them. So, you should work on the sheet of white Benchcote provided, sticking it down at the corners with adhesive tape, shiny side down.

At several places in these experiments you should record the observations and measurements that you make. Do this *directly* into your Notebook so that you have a permanent record.

In several of the experiments you need to use only an approximate amount of substance, so don't spend much time measuring these amounts. You can use the measuring spoon in the Kit. One 'spoon' of substance is a level spoonful in this measuring spoon.

This experiment is in three parts, and each of the first two parts provides the substance for the next.

Part 1

First follow the instructions in the *Experiment Kit booklet 2* concerning the assembly and use of the burner.

Set up the apparatus for heating the crucible as shown in Figure 2. Measure two spoons of copper powder into the porcelain crucible. Take the spatula and use it to stir the copper powder, without having your hand directly above the burner (Figure 3). Now adjust the gas burner so that the air holes are half open, as shown in Figure 4. The air inlet to the burner controls the temperature of the flame. Open the gas supply, light the burner and heat the crucible for about two minutes while stirring the powder with the spatula.

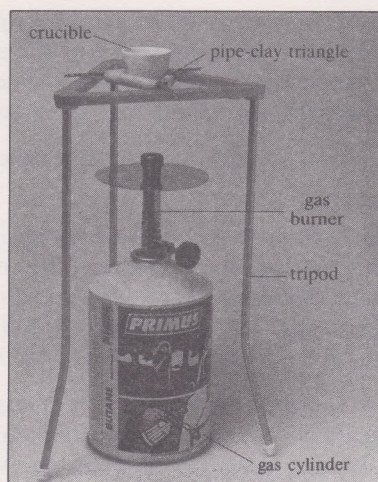


FIGURE 2 Heating the crucible in Experiment 1.

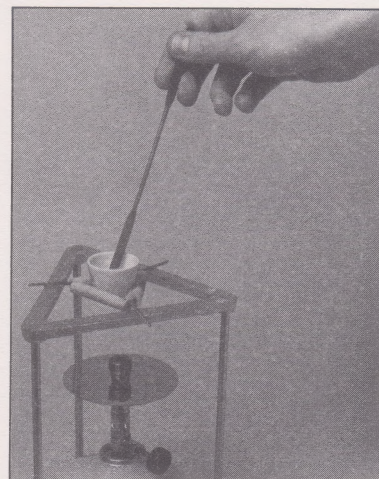


FIGURE 3 Stirring with the bent spatula.

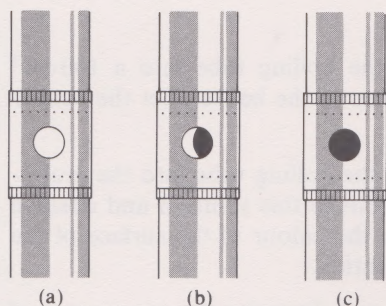


FIGURE 4 The air inlet for the gas burner, (a) closed, (b) half open and (c) fully open.

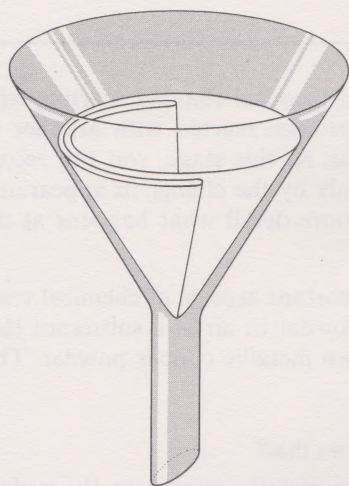


FIGURE 5 A folded filter paper in a funnel.

Observe and record in your Notebook any changes in the powder as it is heated. (You may notice some vapour or smoke evolved. This is due to water or some other impurity in the powder.) Complete this part by opening the air holes fully to give a hotter flame and continue to heat the crucible without stirring for about five minutes.

Meanwhile prepare for the next part. Place a boiling tube in the test-tube rack and put the filter funnel into the tube. Fold a piece of filter paper into half and half again to make a quadrant. Open one thickness of the paper so that it forms a cone that will fit the funnel (Figure 5). Put the paper cone into the funnel and wet it with water so that it clings to the glass. Replace the funnel in the boiling tube, and set the test-tube rack to one side.

Part 2

Return to the crucible, turn off the gas burner and allow the powder to cool for a few minutes. Fold a piece of paper in half to make a chute. Now lift the crucible with the tongs (Figure 6) and tip the contents onto the paper. You may need to scrape out the powder with the spatula, but do not worry if you cannot remove all of the powder.

CAUTION—the crucible will still be hot and you will burn your fingers if you touch it.

Using the folded paper as a chute, pour the powder into your second and empty tube. Add about 5 cm^3 of dilute hydrochloric acid to this tube (5 cm^3 corresponds to about 2 cm depth in the boiling tube).

Relight the burner with the air holes half open and heat the boiling tube, while holding it with the tube tongs (Figure 7), until the liquid just boils. Keep the mouth of the boiling tube pointed away from yourself and anyone else in the vicinity. Shake the tube gently in the flame to keep the liquid boiling gently and evenly for about one minute. Now pour the contents, liquid and powder, into the paper cone in the filter funnel, and allow the liquid to filter into the tube below. Turn off the gas burner.

Examine the contents of the filter paper and boiling tube and record their appearances. You can now discard the filter paper and its contents.

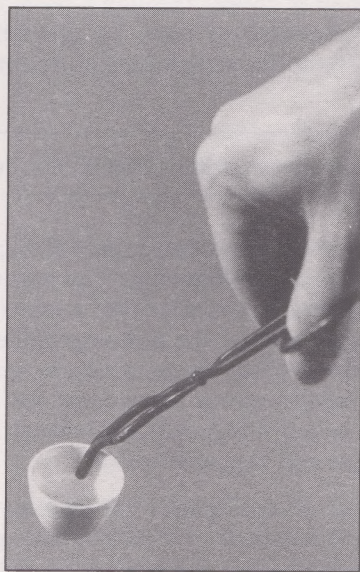


FIGURE 6 Holding the crucible with tongs.

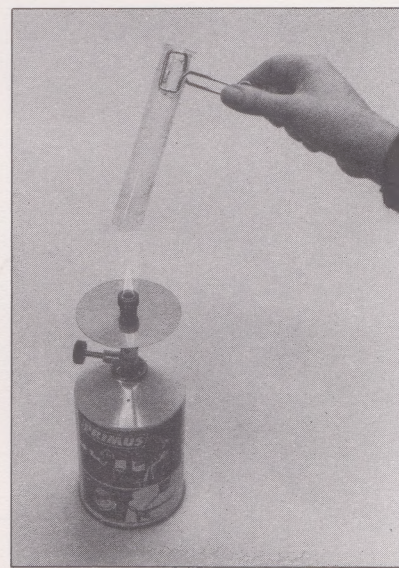


FIGURE 7 Heating a boiling tube.

EXPERIMENT
CONTINUED

Part 3

Pour about half of the solution from the boiling tube into a 100 cm³ beaker and add a wire nail to the solution in the beaker. Set the beaker aside for a few minutes.

Now pour the remaining solution from the boiling tube into the evaporating basin. Add a small ball of zinc wool to this solution and observe any changes that occur. Note especially the colour of the surface of the wool and eventually the colour of the solution.

Return to the beaker that contains the nail. Examine the appearance of the nail and record this in your Notebook.

You can now discard the zinc wool, and wash out your apparatus. Clean your crucible with a scouring pad if necessary. If you wish, keep the wire nail as a souvenir!

 CONSERVATION OF
ELEMENTS

 CHEMICAL STRUCTURE

 MOLECULE

 CHEMICAL REACTION

 REACTANT

 PRODUCT

In Experiment 1, you have observed several chemical changes, starting with copper. In each of these changes, one substance reacted with another to produce a different substance or substances. At this stage, you can recognize these changes as chemical reactions only by the change in appearance that occurs. Shortly we shall describe in more detail what happens at the atomic level in chemical reactions.

The experiment also introduces several important aspects of chemical reactions. First, the result of heating copper powder in air is a substance that looks quite different from the reddish-brown metallic copper powder. This substance nevertheless contains copper.

☐ Which observation in Experiment 1 shows this?

■ In Part 3, the recovery of reddish-brown metallic copper on the surface of the zinc tells you that copper is present at each stage of this experiment, although not always as the metal.

In fact, the dark substance made in Part 1 was produced by a combination of copper with oxygen in the air. Some of the copper remains uncombined and this appears as the reddish-brown residue in the filter paper in Part 2 of the experiment. The reappearance of copper at the end of the experiment also shows that copper is conserved throughout the experiment and so is present in the solution obtained in Part 2. This observation about the preservation of copper through a series of its reactions is true for all elements in their chemical reactions. To generalize from this, we can state the following rule about the **conservation of elements**:

Elements are neither created nor destroyed in chemical reactions.

The second important aspect of Experiment 1 concerns the meaning of the term chemical compound. The product of the first reaction is the compound of copper and oxygen called copper(II) oxide. (At this stage you need not be concerned about the meaning of the Roman number II.) When we say that copper(II) oxide contains copper and oxygen, we mean that copper atoms and oxygen atoms are present but they are combined in an intimate way. This is best illustrated by showing the arrangement of the atoms in copper, oxygen and copper(II) oxide.

As you saw in Figure 1, the element copper contains only one kind of atom. Copper is typical of metals in having each atom surrounded by a number of other atoms in a regular fashion, with the pattern shown in Figure 1 repeating to give a large array of atoms in each crystal of copper. Each copper atom is surrounded in this large array by twelve identical copper atoms. The arrangement of atoms in a substance, as shown in Figure 1, is called its **chemical structure**.

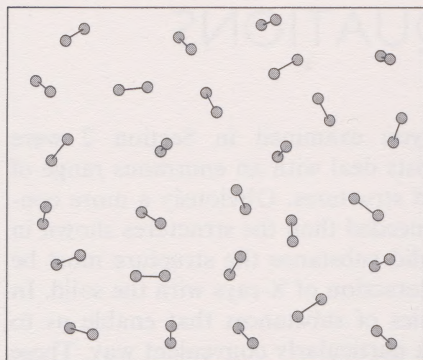


FIGURE 8 Oxygen molecules in a gas. The molecules move randomly and independently.

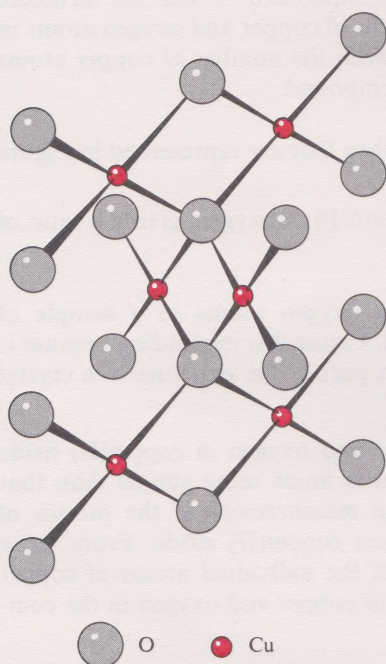


FIGURE 9 The arrangement of copper and oxygen atoms in copper(II) oxide.

In oxygen, the gas consists of small particles of oxygen each containing two atoms of oxygen joined together. Small groups of atoms joined in this way are called **molecules**. In oxygen gas, the identical molecules move independently and in random directions—as Figure 8 implies, they have no regular arrangement.

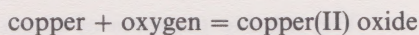
In copper(II) oxide, each copper atom is surrounded by four oxygen atoms, and each oxygen atom is surrounded by four copper atoms (Figure 9). As with copper, the pattern extends to a large array to form a crystal.

So the chemical compound that you first produced is not a random mixture of copper and oxygen. It contains a *regular arrangement* of copper and oxygen atoms joined to each other. The change that you observed, from reddish-brown metal to black powder, is even more striking at the atomic level. It is the arrangement of atoms that characterizes chemical compounds and distinguishes them from mixtures. In mixtures the atoms of the various components have no fixed relationship to each other.

It is the *change* in the arrangement of atoms that characterizes a **chemical reaction**, for example from the separate arrangements of copper and oxygen atoms in Figures 1 and 8 to that in Figure 9.

Two other reactions took place in Experiment 1. The first was the formation of a blue solution when copper(II) oxide dissolves in hydrochloric acid. The solution contains the substance copper(II) chloride, which makes it blue. Finally, there was the formation of copper metal by the reaction of zinc with the solution of copper(II) chloride. The main purpose of performing the experiment was to illustrate the idea that elements (in this case copper) are conserved in chemical reactions. Later, in Section 3, we shall deal with the form that copper takes in the solution of copper chloride.

The reactions that you studied in Experiment 1 also provide examples with which we can introduce a convenient way of representing chemical changes. In the first part of the experiment copper reacted with oxygen to produce copper(II) oxide. We can represent this change in the following way:



The equality sign is meant to show that the substances on the left react to produce the substance on the right. In a chemical reaction the substances that react, those on the left, are called **reactants**. The substances that are produced, on the right, are called **products**. In the next Section you will examine the product of a reaction more closely, and we shall introduce a more convenient way of representing reactions using chemical symbols.

SUMMARY OF SECTION 2

- 1 Elements that take part in a chemical reaction are present in the products: elements are neither created nor destroyed in chemical reactions.
- 2 Chemical compounds contain atoms in a regular arrangement unlike the random arrangement of mixtures.
- 3 Chemical reactions can often be recognized by changes in appearance; the products usually look different from the reactants. At the atomic level, chemical reactions involve a rearrangement of atoms.

SAQ 1 When magnesium reacts with hydrogen chloride (a compound containing hydrogen and chlorine), one product is magnesium chloride (a compound containing magnesium and chlorine). What other product will result from this reaction?

SAQ 2 In what way is the following statement incomplete? 'North Sea gas contains methane (a compound of carbon and hydrogen), which burns in air to produce carbon dioxide (a compound of carbon and oxygen.)'

3 FORMULAE, EQUATIONS AND VALENCY

The substances and reactions that you examined in Section 2 were described in words and pictures. Chemists deal with an enormous range of substances, some with very complicated structures. Obviously a more convenient representation of substances is needed than the structures shown in Figures 1, 8 and 9. Moreover, for a solid substance the structure must be deduced from a lengthy study of the interaction of X-rays with the solid. In this Section we examine some properties of substances that enable us to represent compounds and reactions in a particularly convenient way. These properties can be measured in some simple experiments and you will be doing one such experiment yourself.

3.1 EMPIRICAL FORMULAE

The copper(II) oxide that you made in Experiment 1 has the structure shown in Figure 9. The regular arrangement of copper and oxygen atoms in this structure suggests a relationship between the number of copper atoms and the number of oxygen atoms in the compound.

- ☐ Count the atoms of copper and of oxygen that are represented in Figure 9. What is their ratio?
- The Figure shows 6 atoms of copper and 16 of oxygen, giving a ratio of 3:8.

However, the ratio of copper atoms to oxygen atoms in a sample of copper(II) oxide is not 3:8. In this respect, Figure 9 is misleading because it shows only a small and arbitrarily chosen part of the structure of a crystal of copper(II) oxide.

The relative numbers of atoms of copper and oxygen in copper(II) oxide can be determined by an experiment that is much more simple than that used to establish Figure 9. It entails the measurement of the masses of copper and oxygen that combine to form copper(II) oxide. From these masses and a knowledge of the masses of the individual atoms of copper and oxygen, we get the number of atoms of copper and oxygen in the compound.

- ☐ From your knowledge of this reaction (Experiment 1), can you suggest a problem that might arise in such an experiment?
- The reaction between copper and oxygen was incomplete, as shown by the unreacted copper that did not dissolve in hydrochloric acid.

We shall therefore turn our attention to a different reaction in which two elements combine to form a compound. In the experiment that follows you will make a compound of tin and iodine starting from two elements. From the masses of tin and iodine that react together, and a knowledge of the atomic masses of tin and iodine, you will obtain the relative numbers of atoms present in the compound. It was information of this kind concerning the ratios of atoms in compounds that led to the ordering of the chemical elements in a systematic fashion, as you will see in later Sections.

EXPERIMENT 2

DETERMINING THE FORMULA OF A COMPOUND OF TIN AND IODINE

TIME

about 3 hours

NON-KIT ITEMS

gas cylinder
household rubber gloves (to wear only when disposing of the product)
kettle
matches
Notebook
paper tissues
sandpaper (or emery paper)
scissors
screwdriver (to assemble balance)
sheet of clean paper

KIT ITEMS

Part 1
hand lens
Chemical tray
acetone
iodine (crystals, one jar)
tin foil (one jar; do not substitute this with aluminium foil, as it is not the same)
1,1,1-trichloroethane
Tray A
test-tubes (twelve)
watch-glass, 75 mm
Tray B
beaker, 250 cm³
beaker, 1000 cm³
condenser cone
filter funnel
measuring cylinder, 25 cm³
round-bottomed flask, 250 cm³
Tray C
balance
balance brush
Benchcote paper
boss-head
ceramic gauze
clamp
crocodile clips (two)
nozzle for gas burner
pipe-cleaners
retort stand base
retort stand rod
safety goggles
screw-cap jar
spatula
test-tube rack
tripod

AIM

The purpose of this experiment is to determine the relationship between the masses of tin and iodine that combine to produce a compound of the two elements. This will enable you to find the ratio of the numbers of tin and iodine atoms in the compound that is formed.

WARNING During this experiment you must wear safety goggles (or your own spectacles). Also remember to wash your hands if you get any chemicals on them and when you finish the experiment. The vapour of 1,1,1-trichloroethane is irritating to the eyes and may be harmful if inhaled, but the condenser should prevent any vapour escaping into the room. In any case, you must work in a ventilated area, except when you are using the balance.

PROCEDURE

First, set up the balance as described in the *Experiment Kit booklet 2* and familiarize yourself with its operation.

Set up the apparatus as shown in Figure 10, but without putting water in the 1000 cm³ beaker, which acts as a water-bath. In Figure 10, note that what we refer to as the condenser consists of the condenser cone together with a test-tube that fits inside the cone. This test-tube is then filled with cold water, and acts as a 'cold finger' on which vapour will condense. Wind a pipe-cleaner once around the top of this test-tube and twist the ends to secure it tightly. Clip a crocodile clip onto the test-tube and over the pipe-cleaner (see inset in Figure 10). For safety reasons, you must use

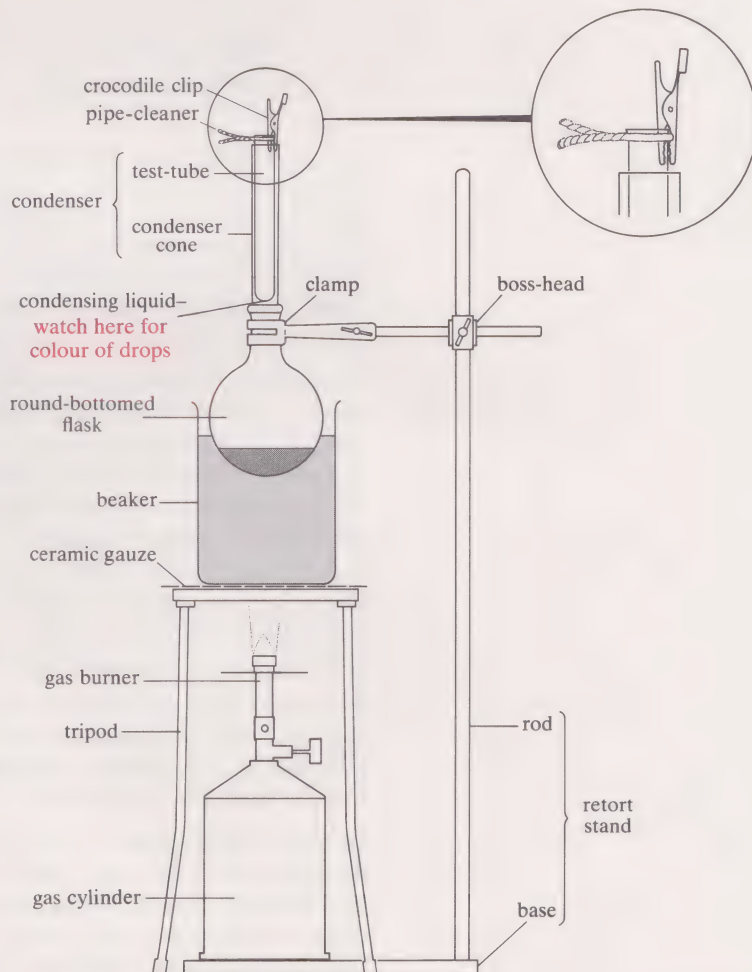


FIGURE 10 The apparatus set up for Experiment 2.

EXPERIMENT
CONTINUED

both of these devices to ensure that the test-tube does not slip through the condenser cone into the flask and break it.

Insert the cold finger into the condenser cone by holding the top of the test-tube. Do *not* use the crocodile clip to remove the cold finger from the cone.

Make sure that the clamp holds the neck of the flask not the condenser cone; the cone will sit in the flask, but an unsupported flask would fall.

The 'cold finger' for the condenser should be filled to within about 1 cm of its rim with cold water from the tap. It is important to exclude water from the chemical reaction, so make sure that the flask and condenser cone are dry inside and that the outside of the cold finger is dry. You will need to change the cold finger often during the experiment, so have a set of test-tubes filled with cold water, ready in the rack. Keep a pipe-cleaner and a crocodile clip on the first one so that it is ready for use. You will need hot water at the start of the reaction so set a kettle to boil while you proceed.

Copy Table 1 into your Notebook, and then prepare the materials for the experiment as follows.

TABLE 1 Results of Experiment 2

mass of paper + iodine	=	g
mass of paper	=	g
mass of iodine used	=	g
mass of tin taken	=	g
mass of residual tin	=	g
mass of tin used	=	g
appearance of product:		

Cut the length of tin foil lengthwise into two strips. Clean the pieces of tin foil by rubbing them on both sides with the sandpaper until they are very scratched. Coil each piece of tin foil around a pencil to obtain a long spiral and place both pieces of tin on the balance pan. Determine the mass of this tin accurately (to within 0.01 gram) and record it in Table 1 in your Notebook. The mass should be between 4 and 5 grams. Remove the tin from the balance pan and set it to one side.

Now measure about 3 g of iodine as follows. Cut a square of shiny paper about 10 cm by 10 cm from the benchcote, and fit it on to the pan of the balance. Determine the mass of this paper to within 0.01 g, and record it in Table 1. Move the rider on the balance beam to the 5 g position. Now use the spatula to put some iodine crystals on the paper on the pan, until the beam is roughly balanced. It does not matter whether the mass of paper plus iodine is slightly more or slightly less than 5 g, but you must know the mass accurately. Balance the beam and determine the mass to the nearest 0.01 g and record it in Table 1. The difference between these last two masses is the mass of iodine.

Remove the condenser from the neck of the flask and put it in the test-tube rack. Put the funnel into the flask, then gently fold the paper so that it bends in the middle, and carefully tip the iodine crystals into the funnel. Brush any crystals that stick to the paper into the funnel.

Measure about 25 cm³ of 1,1,1-trichloroethane into the measuring cylinder and pour it into the funnel, so that the crystals of iodine are washed into the flask. Repeat with another 25 cm³ portion, making 50 cm³ in all. Some of the iodine will dissolve. Notice the colour of the solution and record this in your Notebook. Remove the funnel, and add both pieces

of tin to the flask. Ensure that the tin is as completely immersed as possible, by swirling the flask if necessary. Return the condenser cone with its cold-finger test-tube to the flask and lower the flask into the beaker by lowering the clamp until the flask is at about the level shown in Figure 10.

Now pour hot water carefully over the flask so that the water fills the beaker to the same level as the solution in the flask. Light the gas burner below the tripod and open the air holes in the burner fully.

When the water in the bath approaches boiling, the liquid in the flask will begin to boil. The vapour will condense on the cold finger and the resulting liquid will run back into the flask. When this happens, the contents of the flask are said to *reflux*. You can control the rate of reflux by raising or lowering the flask in the hot water. To do this, adjust the position of the clamp on the stand. Ideally the condensing liquid should run from the cold finger at the rate of about one or two drops a second. The water in the bath should not be allowed to boil vigorously although it may simmer. Control this by adjusting the gas burner.

As the liquid refluxes, the water in the cold finger gets hot and you will notice that the level of the condensing liquid rises on the outside of the cold finger. When it reaches about 2 cm from the top of the condenser cone it is time to change the cold finger. Have ready a new cold finger, complete with pipe-cleaner and crocodile clip. You will need to make the change quickly to prevent fumes of solvent and iodine escaping from the cone. Remember that it is important to exclude water from the flask so check that your new cold finger in the test-tube rack is dry on the outside.

Lift the heated cold finger from the sleeve, and insert the new cold finger with its pipe-cleaner and crocodile clip into the sleeve. You will find that you need to replace the cold finger about every three or four minutes, depending on the rate of reflux. Make sure that you always have a new cold finger with pipe-cleaner and crocodile clip ready to replace the one in use.

When the liquid refluxes, some iodine is carried in the vapour to the cold finger. As the reaction proceeds, the iodine is used up. You should watch carefully the colour of the liquid drops at the bottom of the cold finger (**not** the colour of the liquid in the flask). The colour of the liquid drops will fade during the reaction. Eventually the drops of condensing liquid become pale pink or even colourless, indicating that there is virtually no iodine left unreacted in the flask. Now it is time to stop the reaction. The reaction time should have been 40 to 60 minutes but it may be longer. Use the colour of the drops to decide. *Remember to watch the colour of the drops, not the colour of the liquid in the flask. (CAUTION Turn off the gas burner now because you will shortly be using acetone, which is a highly flammable solvent.)*

When the reaction is complete, loosen the boss-head and remove the flask and clamp from it (you can hold the hot flask by the clamp). Remove the condenser and put it in the test-tube rack, and quickly examine the contents of the flask. Do not allow the flask to cool before proceeding.

- ☐ Is there any solid that remains unreacted, and if so, what does it look like?
- ☒ Provided that you took the amounts of tin and iodine suggested, there should be some unreacted tin at the bottom of your flask. You now have to determine the mass of this unreacted tin.

While holding the clamp, tip the flask, and carefully and slowly pour the hot liquid from the flask into the 250 cm³ beaker, so that the tin remains in the flask. When most of the liquid is transferred, pour very slowly to avoid transferring any tin to the beaker. This procedure for separating a

EXPERIMENT
CONTINUED

liquid from a denser solid is called *decantation*. Pour the liquid into the screw-cap jar and set it aside.

The flask now contains the tin that did not react and some of the product dissolved in some residual liquid. You need to separate the tin from this product by washing it with acetone. Pour about 20 cm³ of acetone from the measuring cylinder down the inside wall of the flask to rinse all of the product to the bottom. Return the clamp to the boss-head and clamp it with the flask in the hot water for two minutes. Now decant the acetone into the 250 cm³ beaker (CAUTION *Acetone is highly flammable*).

Repeat this washing of the residual tin twice more with further 20 cm³ portions of acetone, again warming the flask in the hot water.

After the residual tin has been washed three times, tip it from the flask onto a clean piece of paper. Spread the tin out and carefully wipe both sides of the foil with a clean tissue. The tin will not become very shiny, but you should remove any residual coloured product from its surface. Be careful not to break up the thinned foil and so lose any pieces. Now check the zero of the balance, put the tin into the pan and record its mass in Table 1.

You now have the data you require: the masses of iodine and tin that have reacted together. The mass of the tin is obtained by taking the difference between the masses of tin present before and after the reaction.

Cool the screw-capped jar that you set aside (it may already be cool) by running tap-water down the outside. You should see that the product has crystallized. Use your spatula to withdraw one or more of the crystals and put them onto the watch-glass.

Examine the crystals with the hand lens and note that the substance has a strikingly different appearance from both tin and iodine. Record the appearance of these crystals in your Notebook. When you have finished observing this product, pour it back into the 250 cm³ beaker and dispose of the contents of the beaker according to the 'Disposal of chemical residues' instructions in the Kit booklet.

CHEMICAL COMPOSITION

EMPIRICAL FORMULA

CONSERVATION OF MASS

The results of Experiment 2 give the relative masses of the two elements tin and iodine contained in the product. This is called the **chemical composition** of the product. From this composition, we can obtain the relative numbers of atoms of tin and iodine that combine in the product. For example, to convert the mass of tin that reacted into the number of atoms, we must divide the mass of the tin by the mass of one atom of tin. This mass is denoted by m_{Sn} and is equal to 197.1×10^{-24} g.

☐ How many atoms are present in 1 g of tin?

☒ The number of atoms is equal to 1 g divided by the mass of one atom.

$$\text{Thus, number of atoms} = \frac{1 \text{ g}}{197.1 \times 10^{-24} \text{ g}} = 5.07 \times 10^{21}$$

Notice the numbers in this calculation. The mass of an atom is extremely small, so there are a huge number of atoms present.

The mass of one atom of iodine is known to be 211×10^{-24} g. Now determine the number of atoms of tin and iodine in the product of your experiment and express this as a ratio. If you are unable to do this, look at the specimen calculation below for a similar experiment. Now complete the calculation and enter the result in your Notebook.

Specimen calculation

When 0.50 g of zinc (Zn) is heated strongly in air, it combines with oxygen (O) to produce a white substance called zinc oxide, which has a mass of 0.62 g. What is the ratio of the number of atoms of zinc to the number of atoms of oxygen in zinc oxide, given the following atomic masses?

$$\begin{aligned}
 \text{mass of one atom of zinc} &= 108.6 \times 10^{-24} \text{ g} \\
 \text{mass of one atom of oxygen} &= 26.6 \times 10^{-24} \text{ g} \\
 \text{mass of zinc} &= 0.50 \text{ g} \\
 \text{mass of oxygen} &= 0.62 \text{ g} - 0.50 \text{ g} \\
 &= 0.12 \text{ g} \\
 \text{number of atoms of zinc} &= \frac{0.50 \text{ g}}{108.6 \times 10^{-24} \text{ g}} = 4.6 \times 10^{21} \\
 \text{number of atoms of oxygen} &= \frac{0.12 \text{ g}}{26.6 \times 10^{-24} \text{ g}} = 4.5 \times 10^{21} \\
 \frac{\text{number of atoms of Zn}}{\text{number of atoms of O}} &= \frac{4.6 \times 10^{21}}{4.5 \times 10^{21}} \approx 1.0
 \end{aligned}$$

This ratio is obviously very close to one, and certainly, within the possible uncertainty limits in such an experiment, we can say that it is one. In the vast majority of chemical compounds, including all of those that are described in these Units, the ratios of atoms of various kinds are ratios of simple whole numbers.

We can express the composition of a compound very conveniently by an **empirical formula**, which shows the kinds and relative numbers of atoms in the compound as determined from its composition: hence the use of the word ‘empirical’, which means ‘from an experiment’ and not based on theory. For example, the oxide of zinc can be expressed as Zn_1O_1 , where the subscripts show the relative numbers of each type of atom present in the compound. Usually, we omit the subscript if it has the value of one, and so we write the empirical formula as ZnO , which indicates that the compound contains equal numbers of atoms of zinc and oxygen.

At this stage, it is worth considering what you have done in determining the formula of this substance.

- ☐ Can you think of any assumptions that were made in the specimen calculation to determine the formula of ZnO ?
- ☒ You might list the following, which are the most important.
 - 1 The two elements reacted to produce only one compound.
 - 2 The product contains only zinc and oxygen. Since we ask you to accept this as a fact, it is not strictly an assumption. It could, of course, be checked by attempting to determine by other methods the oxygen content of the oxide. Zinc plus oxygen should account for 100% of the oxide if the compound contains only these two elements.
 - 3 No zinc or zinc oxide was lost in the experiment. Since neither of the substances is volatile, this assumption should depend only on whether any substance was spilled in the experiment, or was lost when the zinc was heated.
 - 4 Mass is conserved in the experiment. Because 0.62 g of product was formed, it was assumed that 0.62 g of reactants had reacted. This allowed calculation of the mass of oxygen that reacted. **Conservation of mass** is an important assumption in chemical reactions and one that is based on the study of very many chemical reactions in which mass is always found to be conserved.
 - 5 Neither the total number of atoms nor their type changes in the reaction. Again this is an important assumption that is made by chemists when performing reactions and when using chemical formulae to represent chemical reactions.

Notice that this last assumption clearly distinguishes chemical reactions from nuclear reactions (Units 11–12). In a nuclear reaction, the combinations of protons and neutrons in the reactants are broken up and the particles are redistributed among the products.

RELATIVE ATOMIC MASS, A_r
MOLE
AVOGADRO'S CONSTANT, N_A
MOLAR MASS, M
AMOUNT OF SUBSTANCE

ITQ 1 When 4.00 g of iron powder (Fe) are heated in air, it combines with oxygen to give a red product with a mass of 5.72 g. What is the empirical formula of this product? (The atomic masses are $m_{\text{Fe}} = 92.7 \times 10^{-24}$ g, $m_{\text{O}} = 26.6 \times 10^{-24}$ g.)

In the calculations that you have made to determine empirical formulae from the masses of reactants and products, you have calculated in each case the number of atoms involved. Of course, atoms are *very* small, and, as you saw in your calculations, the numbers of atoms in your experiment are very large.

In most practical problems it is inconvenient to deal with such large numbers of atoms. To overcome this problem, chemists use a scale of **relative atomic masses**, which is based on one element. You know from Units 11–12 that the hydrogen atom is the lightest atom; it consists of one proton and one electron, and has a mass number of 1. Heavier atoms contain integral numbers of protons and neutrons. Protons and neutrons have almost equal masses, so the masses of other atoms are very nearly integral multiples of the mass of a hydrogen atom. A sensible choice of scale for relative atomic masses would be one in which the relative atomic mass of hydrogen is set at exactly 1. In fact such a scale was originally chosen, and the modern scale is not very different from it. But for convenience carbon is now used as the standard element. You also know from Units 11–12 that elements usually consist of more than one isotope. It is important therefore to specify which isotope is selected as the standard. The standard chosen is the most abundant isotope of carbon, ^{12}C . By definition, the relative atomic mass of the isotope ^{12}C is set at *exactly* 12.

A Table of the relative atomic masses of the elements is given in Appendix 1, correct to three significant figures. The relative atomic mass of carbon was quoted more precisely in Units 11–12 as 12.011 15. The values in Appendix 1 of Units 11–12 give the relative atomic masses of the elements as they occur naturally. Carbon consists of more than one isotope: it contains small proportions of ^{13}C and ^{14}C , although it is mainly ^{12}C . The value of its relative atomic mass is therefore a little more than 12.

The experiment that you performed with tin and iodine is typical of experiments that have been used to determine the ratios of atoms in compounds. Chemists typically work with quantities of substances that they measure in grams. For this reason, we introduce a unit that is often more useful than the mass itself. This unit is the **mole**, and it too is defined in relation to the isotope ^{12}C . A mole of ^{12}C is that amount of the isotope ^{12}C that contains exactly 12 g of ^{12}C .

□ If the mass of *one* atom of ^{12}C is $1.992\,6 \times 10^{-23}$ g, how many atoms of carbon are present in one mole (12.000 g) of ^{12}C ?

■ The number of atoms in one mole of ^{12}C is

$$\frac{12.000\text{ g}}{1.992\,6 \times 10^{-23}\text{ g}} = 6.022 \times 10^{23}$$

This number has particular importance. A mole of an element is the amount of that element that contains exactly this number of particles; for example:

1 mole of helium is 6.022×10^{23} atoms of helium

1 mole of zinc is 6.022×10^{23} atoms of zinc

The number of particles per mole of an element is a constant. It is called the **Avogadro constant** and is given the symbol N_A . It has the units of mol^{-1} , usually abbreviated as mol^{-1} :

$$N_A = 6.022 \times 10^{23}\text{ mol}^{-1}$$

Because a mole contains such a large number of entities, it is not usually a convenient unit for counting. A mole of people exceeds the total population

of the world by a factor of more than 10^{14} ! However, it is a convenient unit with which to count atoms in chemical substances. When chemists study the transformations involved in chemical reactions, they often measure the masses of the reactants used and of the products formed. These masses, as we said, are usually reported in grams. Most of the calculations involving chemical substances make use of moles. So it is important that you are able to convert the moles into mass, and vice versa. The mass of one mole of a substance is called the **molar mass**, M , of that substance. To convert from mass in grams into moles, simply divide by the molar mass, which has the unit g mol^{-1} . For example, 1 mole of ^{12}C has a mass of 12 g, so its molar mass is 12 g mol^{-1} . A mass of 6 g of ^{12}C is therefore equal to

$$6 \text{ g} / 12 \text{ g mol}^{-1} = 0.5 \text{ mol}$$

Experiments in chemistry almost invariably involve elements containing their natural abundances of isotopes. Therefore we use the Table of relative atomic masses (Appendix 1) to determine the molar masses of elements as they occur naturally. Remember that these relative atomic masses are for the naturally abundant ratios of isotopes and that they are based on ^{12}C isotope.

- ☐ What is the molar mass of naturally occurring iron?
☒ According to the Table in Appendix 1, the relative atomic mass of iron is 55.8. The molar mass is therefore 55.8 g mol^{-1} .

The number of moles in a particular sample of a substance is called the **amount of substance**. Thus, the amount of iron that has a mass of 55.8 g is 1 mole.

ITQ 2 Use the relative atomic masses from Appendix 1 to calculate the amount of the respective elements contained in (a) 100 g of helium and (b) 100 g of iron.

In general, it is much more convenient to deal with moles of substance rather than numbers of atoms when performing the sort of calculation that you made in determining the empirical formula of the product in Experiment 2. For example, consider the following calculation based on a study of the first compound that you made in Experiment 1. When 2.00 g of copper react completely with oxygen, the product has a mass of 2.50 g. What is the empirical formula of the product?

First, the masses are converted into amounts of substance (moles) by dividing by the relative atomic masses. The amount of copper is given by

$$\begin{aligned} \frac{\text{mass of copper}}{\text{molar mass of copper}} &= \frac{2.00 \text{ g}}{63.5 \text{ g mol}^{-1}} \\ &= 3.15 \times 10^{-2} \text{ mole of Cu atoms} \end{aligned}$$

Notice that for oxygen we must use the relative atomic mass of 16.0 because we want the relative number of atoms (O), and not the relative number of molecules (O_2). So the amount of oxygen is given by

$$\begin{aligned} \frac{\text{mass of oxygen}}{\text{molar mass of oxygen}} &= \frac{0.50 \text{ g}}{16.0 \text{ g mol}^{-1}} \\ &= 3.13 \times 10^{-2} \text{ mole of O atoms} \end{aligned}$$

To find the empirical formula we find the smallest integers whose ratio equals the ratio of the numbers of moles.

$$\begin{aligned} \frac{n(\text{Cu})}{n(\text{O})} &= \frac{3.15 \times 10^{-2}}{3.13 \times 10^{-2}} \\ &= 1 \text{ (very nearly)} \end{aligned}$$

The empirical formula is therefore CuO.

MOLECULAR FORMULA

GAY-LUSSAC'S LAW

AVOGADRO'S LAW

PHASE

CHEMICAL EQUATION

To take another example, we find that 6.35 g of copper react with 3.21 g of sulphur (S) to give a black compound. These masses can readily be converted into amounts of substance (in units of moles):

$$\text{amount of copper} = \frac{6.35 \text{ g}}{63.5 \text{ g mol}^{-1}} = 0.100 \text{ mole of Cu atoms}$$

The number of moles of sulphur atoms is

$$\frac{\text{mass of sulphur}}{\text{molar mass of sulphur}} = \frac{3.21 \text{ g}}{32.1 \text{ g mol}^{-1}} = 0.100 \text{ mole of S atoms}$$

From this we can conclude that 1 mole of copper combines with 1 mole of sulphur. In other words, the black compound contains copper atoms and sulphur atoms in the ratio 1 : 1, and its empirical formula is therefore CuS.

ITQ 3 It is found that 24.02 g of carbon react with 64.00 g of oxygen. What is the empirical formula of the product?

SAQ 3 When 3.00 g of copper react completely with chlorine (Cl) the product has a mass of 6.40 g. What is the empirical formula of the product?

SAQ 4 Silver (Ag) occurs as an ore silver sulphide, which is a compound with sulphur (S): 10.0 g of this sulphide are found to contain 8.70 g of silver. What is the empirical formula of the silver sulphide?

SAQ 5 Mercury (Hg) forms a red oxide. When 5.00 g of this oxide are heated it decomposes to produce oxygen and mercury. If 4.63 g of mercury are formed, what is the empirical formula of the mercury oxide?

3.1.1 MOLECULAR FORMULAE

So far, our discussion has been concerned with empirical formulae. These formulae give the *ratios* of atoms that combine in chemical compounds. They are determined by measuring the chemical composition of a compound. Thus, copper(II) oxide contains equal numbers of copper and oxygen atoms, so its empirical formula is CuO. This formula, however, gives no information about the structure (the arrangement of atoms) of copper(II) oxide that is shown in Figure 9.

Oxygen exists as a gas whose structure is represented in Figure 8. The particles consist of two atoms joined together to form a molecule. The molecules of a gas are distributed randomly. It would be misleading to represent an oxygen molecule by the symbol O; instead we represent it by the symbol O₂, which is its **molecular formula**. Iodine also exists as molecules that contain two atoms, in the purple vapour, in solution and in the dark solid. Thus iodine is also a diatomic molecule and is represented as I₂.

Our knowledge of molecules stems from experiments made at the beginning of the 19th century on the reactions of gases, and from two laws that emerged from these experiments.

The first of these is **Gay-Lussac's law**. Gay-Lussac was a French chemist who observed that when gases react with each other the volumes of the reacting gases and of the products, if these are gases, are in a ratio that can be expressed by small whole numbers. For example, the gas hydrogen reacts with gaseous chlorine to give hydrogen chloride, another gas. We find that 1 cm³ of hydrogen gas reacts with 1 cm³ of chlorine gas to give 2 cm³ of hydrogen chloride gas, if the volumes are all measured at the same temperature and pressure. Gases change their volumes if either temperature or pressure is changed, so in these experiments the volumes must all be measured at the same temperature and pressure.

The second law, proposed by the Italian chemist Avogadro, provides an explanation of the first. According to **Avogadro's law**, equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. In the example of hydrogen and chlorine, equal numbers of molecules of these gases react to produce *twice* this number of molecules of

hydrogen chloride. We can represent the reaction by the following statements. First, in accordance with Gay-Lussac's law:

1 cm³ of hydrogen plus 1 cm³ of chlorine produce 2 cm³ of hydrogen chloride; that is, the volumes are in the simple integral ratio 1 : 1 : 2.

According to Avogadro's explanation:

One molecule of hydrogen plus one molecule of chlorine produce two molecules of hydrogen chloride.

TABLE 2 Substances consisting of diatomic molecules

Substance	Formula
oxygen	O ₂
nitrogen	N ₂
hydrogen	H ₂
fluorine	F ₂
chlorine	Cl ₂
bromine	Br ₂
iodine	I ₂

Obviously, the smallest number of atoms of hydrogen that can be present in a molecule of hydrogen chloride is one. So if *one* molecule of hydrogen produces *two* molecules of hydrogen chloride, it follows that a molecule of hydrogen must contain *at least two* atoms of hydrogen. In fact, it does contain two atoms and we represent it as H₂. The same logic leads to the conclusion that a molecule of chlorine contains at least two atoms. The molecule actually contains two atoms and we represent it as Cl₂.

Some important *molecular* formulae that you need to know are those of the diatomic gases and the elements bromine and iodine, which also exist as diatomic molecules. These appear in Table 2.

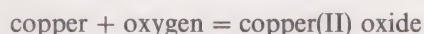
Chemical formulae provide a convenient means of representing chemical substances. However, the chemical formula alone does not indicate the form in which the substance occurs. Water, for example, exists as a solid (ice), a liquid and a gas (steam). We call these different forms of substances their **phases**. It is often useful to indicate the phase of a substance when writing its formula, and this is done by adding the appropriate letter in brackets immediately after the formula: (s) denotes a solid, (l) denotes a liquid and (g) denotes a gas. Thus, liquid water is represented by the symbol H₂O(l), ice by H₂O(s), and steam by H₂O(g).

SAQ 6 When hydrogen and oxygen react to produce water at a temperature higher than that at which water condenses, 2 cm³ of hydrogen react with 1 cm³ of oxygen to produce 2 cm³ of steam (gaseous water). (i) Explain how this observation supports the notion that oxygen exists as diatomic molecules. (ii) What is the molecular formula of water? (iii) Write formulae for the substances in this reaction, and indicate their phases.

SAQ 7 A compound with the empirical formula CH has a molar mass of 26 g mol⁻¹. What is its molecular formula?

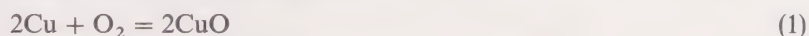
3.2 CHEMICAL EQUATIONS

In Experiment 1 you observed that copper reacts with oxygen to produce copper(II) oxide. Chemists usually represent a reaction by writing a **chemical equation**. The reaction is written with the reactants on the left of an equality sign and the products on the right. In this case the reaction can be represented as



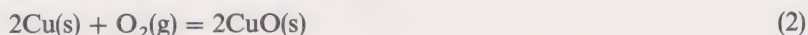
If, however, the masses of copper and oxygen that combined chemically to produce copper(II) oxide have been measured, we know how many atoms of copper and how many molecules of oxygen took part in the reaction.

The ratio of the reactants can then be represented by their chemical symbols. When this is done, the equation must balance; the atoms that appear on the left-hand side must also appear on the right-hand side. With chemical symbols, the equation becomes



Here O₂ represents a molecule of oxygen, 2Cu represents two atoms of copper and 2CuO represents two atoms of copper and two atoms of oxygen combined in the form of copper(II) oxide. Notice that there are two atoms of copper and two atoms of oxygen on each side of the equation. It *balances*.

Sometimes chemists also include the phase of each substance in the equation for a reaction. Thus, Equation 1 can be written:



To take another example, consider the reaction of hydrogen with oxygen to produce water (SAQ 6). Using the formulae H_2 , O_2 and H_2O for the three substances, we begin by writing the formulae of the reactants and products.



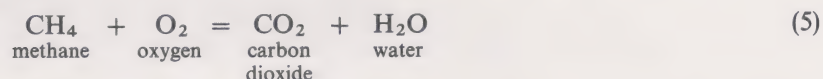
Does the equation balance?

It obviously does not balance—there are two oxygen atoms on the left side and only one on the right. To balance the two oxygen atoms, two molecules of water are needed on the right, and this in turn requires two molecules of hydrogen on the left. The balanced equation is



Note that a 2 in front of a formula means two of everything. Thus $2\text{H}_2\text{O}$ means two molecules of water, which of course contain four atoms of hydrogen and two atoms of oxygen. On the other hand, the subscript 2 after the symbol H implies that each water molecule contains two atoms of hydrogen.

Now consider a less simple example: the combustion of methane (CH_4) in oxygen (O_2) to produce carbon dioxide (CO_2) and water (H_2O). This example illustrates how to balance an equation when several substances have to be considered. Start by writing the formulae of reactants and products:



This equation does not balance, and so the use of the 'equal to' sign is not really correct at this stage. Before attempting to balance the equation, it is important to check that the elements that enter the reaction are also present in the products.

☐ Do all the elements on the left of Equation 5 appear on the right?

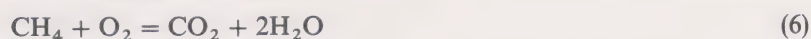
☒ Yes; C, H and O appear on each side.

However, there are not equal numbers of oxygen and hydrogen atoms on each side, although the carbon atoms do balance. You could attempt to balance the expression by trial and error, but it might be some time before you succeeded. Skill at balancing equations comes only with practice, but the task can be made easier if you start with the right atoms. For example, in this expression you should not worry about the number of oxygen atoms when you begin. The reactant molecule oxygen is an element. It contains only one sort of atom, so that you can easily balance the oxygen atoms in your final step merely by changing the number of oxygen molecules on the left. On the other hand, if you introduce more molecules of methane into the expression, you change the numbers of both carbon and hydrogen atoms.

It therefore makes sense to begin with methane. Try first to balance the expression with only one CH_4 molecule.

☐ How many molecules of CO_2 and H_2O are needed on the right-hand side of Equation 5 to balance one molecule of CH_4 ?

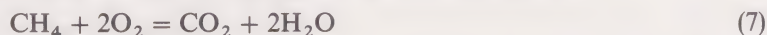
☒ To balance the carbon and hydrogen atoms, one molecule of CO_2 and two molecules of H_2O are required. So we can write Equation 6 with carbon and hydrogen both balanced, although the oxygen atoms remain unbalanced at this stage:



Notice that again we represent two molecules of water by writing a 2 in front of the formula H_2O . It remains to balance the oxygen atoms. This is

now easy because you can adjust the number of oxygen molecules on the left without changing the numbers of any other atoms.

- How many oxygen molecules are required on the left to make the equation balance? Remember that $2\text{H}_2\text{O}$ signifies two molecules of H_2O .
- In Equation 6, there are four oxygen atoms on the right-hand side (two in CO_2 and two in $2\text{H}_2\text{O}$), so four are required on the left. So two molecules of oxygen (2O_2) are required, as in Equation 7.



Equation 7 contains equal numbers of atoms on the left and right. The equation is therefore balanced and the use of the 'equal to' sign is now legitimate.

To ensure that an equation does balance, you should always check that the total number of each type of atom is the same on both sides of the equation.

You should now be able to use balanced chemical equations to represent the reactions that you performed in Experiment 1. The first of these reactions is the conversion of copper into copper(II) oxide (formula CuO) by combination with oxygen in the air, which was represented by Equation 2. The second is the reaction between copper(II) oxide and hydrochloric acid (HCl). The products of this reaction are copper(II) chloride and water (H_2O). In this case, deduce the formula of copper(II) chloride by using the formulae of reactants and the other product in an equation. The oxygen in the water comes entirely from CuO . The third step is the reaction between zinc (Zn) and copper(II) chloride to produce metallic copper and zinc chloride (ZnCl_2).

ITQ 4 Write balanced equations to represent the second and third reactions in Experiment 1.

SAQ 8 The Open University mace, which is carried at graduation ceremonies, is made of the metal titanium, Ti . The final step in the production of titanium is the reaction of titanium(IV) chloride, TiCl_4 , with magnesium (Mg), which forms MgCl_2 . Write a balanced equation to represent this reaction.

SAQ 9 Lamp filaments are made of the metal tungsten (symbol W , from its older name of wolfram). Tungsten is produced by treating the oxide WO_3 with hydrogen to give the metal and water. Write a balanced equation to represent this reaction.

SAQ 10 When the two gases hydrogen sulphide (H_2S) and sulphur dioxide (SO_2) are mixed, they produce liquid water and solid elemental sulphur. Write a balanced equation to represent this reaction, and include the phases of the reactants and products.

3.3 VALENCY

The empirical formulae of very many chemical compounds, including all of those that you will meet in these Units contain small whole numbers representing the relative numbers of atoms in the compound. There are important theoretical reasons for these ratios to be small whole numbers, and we shall discuss them in Section 7. Here we focus on the relationship between the numbers of atoms that combine in different compounds. An examination of this relationship leads to a property called valency, which is helpful in predicting the formulae of compounds.

Consider the following three formulae:



VALENCY

Notice that in HCl the elements hydrogen and chlorine combine with each other in the atomic ratio 1:1. *Each* of these two elements combines with nitrogen in the *same* ratio of 3:1 in NH_3 and NCl_3 . There appears to be a relationship between the three formulae. This kind of observation for sets of compounds led chemists to the suggestion that the formula of a compound is determined by some inherent property of the constituent elements. This property, called **valency**, determines the relative numbers of atoms of elements in compounds. If each element had only a single value of its valency, the formulae of compounds could be readily predicted from a knowledge of those valencies. Unfortunately, many elements have several values of valency, which reduces the predictive power of the concept. Nevertheless, it is still possible to predict the formulae of compounds that might be formed by choosing formulae that are consistent with the known values of valency.

We shall return shortly to the notion of variable valency. In the meantime, we shall assume that the valency of an element is fixed, and we shall select our examples accordingly.

The rules for determining the valency of an element are quite simple, particularly for binary compounds (that is, compounds that contain two elements), and we shall restrict the discussion to these compounds. Because valency is based on formulae, it is concerned with the *relative* numbers of atoms in compounds. So, some arbitrary reference element is chosen as the basis of values of valency. This element is hydrogen, and by definition its valency is taken to be one.

If an element forms a binary compound with hydrogen, its valency is equal to the number of atoms of hydrogen that combine with one atom of that element. For example, in HCl one atom of chlorine combines with *one* atom of hydrogen. So the valency of chlorine is one.

- ☐ What valency do you deduce for nitrogen on the basis of its compound with hydrogen, NH_3 ?
- In NH_3 , one atom of nitrogen combines with *three* atoms of hydrogen, so the valency of nitrogen is three.

If the valency of each of the elements does not vary it should be possible to predict the formula of a binary compound. For example, we have concluded that the valency of nitrogen is three (in NH_3) and the valency of chlorine is one (in HCl). With this information, we would expect nitrogen and chlorine to form a compound with the formula NCl_3 , which indeed is the case. Thus, valency has important predictive properties. Moreover, the observation that nitrogen and chlorine combine as NCl_3 shows that it is not necessary to rely on a knowledge of the formula of a compound of hydrogen in order to determine the valency of an element. For example, if the valency of chlorine in HCl is like that of hydrogen, one, the valency of nitrogen is equal to the number of atoms of chlorine that combine with one atom of nitrogen. In NCl_3 , therefore, the valency of nitrogen is three. To take another example, hydrogen and oxygen combine as water, which has the formula H_2O .

- ☐ What is the valency of oxygen in H_2O ?
- One atom of oxygen combines with two atoms of hydrogen, so its valency is two.

In Experiment 1, you produced a black oxide of copper, with the empirical formula CuO.

- ☐ What is the valency of copper in this oxide?
- We have just shown that oxygen has a valency of two. The formula of copper(II) oxide implies that copper has the same valency—two. The valency of copper is equal to *twice* the number of oxygen atoms that combine with one atom of copper.

Earlier we told you not to bother about the meaning of the Roman numeral II in the name copper(II) oxide. This Roman numeral is the value of a

property called the oxidation state of copper in this compound. Oxidation state is a concept that we shall not develop further in these Units, although it is related to valency and thus it is no accident that it has the same value as the valency of copper in this compound.

As the examples above illustrate, the idea that elements have a fixed valency is useful in predicting formulae. In general, if element A has valency x , and element B has valency y , then if A and B combine to form a compound, y atoms of A will combine with x atoms of B.

However, there are limitations to the generality of these predictions and to the information that valency provides. Valency alone gives no indication of the nature of the interaction between atoms. It does not tell us whether a substance is molecular or whether it exists as a solid consisting of an extended array as CuO does (Figure 9). Here we shall explore further the limitations of the predictions that we may make using valency. Thus we now examine the notions of fixed and variable valency in some further experiments with compounds of copper.

SAQ 11 In forming compounds, silicon (Si) generally exhibits a valency of four. What is the empirical formula of the simplest substance that silicon can form with hydrogen?

SAQ 12 Sulphur (S) forms an oxide in which sulphur has a valency of six. What is the empirical formula of that oxide?

SAQ 13 Carbon forms a compound, methane, with the formula CH_4 . On the basis of its valency in methane, what are the formulae of the simplest compounds that carbon should form with (i) oxygen and (ii) chlorine?

EXPERIMENT 3

INVESTIGATING THE VALENCY OF COPPER

TIME

about 30 minutes

NON-KIT ITEMS

gas cylinder
matches
Notebook

KIT ITEMS

Chemical tray
copper(I) oxide powder
copper powder
dilute sulphuric acid (1 mol l^{-1})
Tray A
porcelain crucible
test-tubes (two)
Tray B
filter funnel
Tray C
Benchcote paper
crucible tongs
filter paper
measuring spoon (spatula-type)
nozzle for gas burner
pipeclay triangle
safety goggles
spatula
test-tube rack

PART 1

Examine the red compound copper(I) oxide and the copper powder and compare and note the appearances of the two substances. Note particularly the difference in their colour.

Set the porcelain crucible on the pipe-clay triangle and tripod, as you did in Experiment 1 (Figure 2). Add three 'spoons' of copper(I) oxide to the crucible and heat it from below with the gas burner as in Experiment 1. Stir the powder occasionally with a bent spatula while heating it for about two minutes.

Observe and record in your Notebook any changes that occur to the powder in the crucible while it is being heated. When the crucible has cooled you can discard the powder.

PART 2

Fold a piece of filter paper, place it in the filter funnel and wet it, as you did in Experiment 1 (Figure 5). Put the stem of the filter funnel into a test-tube supported in the test-tube rack.

Add one 'spoon' of copper(I) oxide to another test-tube and add dilute sulphuric acid to a depth of about 1 cm. Shake the tube from side to side for two minutes to mix the contents and pour the contents into the filter paper. The liquid will take several minutes to filter through.

Examine the solution in the test-tube and the residue in the filter paper and record the appearance of these in your Notebook.

NOBLE GASES

ALKALI METALS

HALOGENS

The red powder, copper(I) oxide, is a binary compound of copper and oxygen. When it is heated in air it gives a product that should be familiar to you.

- ☐ Can you suggest from its appearance what this product is?
- ☒ The black powder obtained looks like the copper(II) oxide that you made and used in Experiment 1.

When the red compound was heated you may have noticed that it first formed the black product on its surface. This suggests that the red copper(I) oxide reacts with some component of the air. In fact, it reacts with oxygen in the air and the product is copper(II) oxide, CuO .

Pure copper(I) oxide is difficult to prepare, which is why you were not asked to determine its formula in this experiment. When the pure compound is prepared it is found to contain 88.8% copper and 11.2% oxygen, as measured by mass.

ITQ 5 Use this information, and the Table in Appendix 1, to calculate the empirical formula of copper(I) oxide.

- ☐ What is the valency of copper in red copper(I) oxide?
- ☒ Again the valency of oxygen is assumed to be two. From the formula Cu_2O , which you deduced in ITQ 5, the valency of copper in Cu_2O is *twice* the number of oxygen atoms ($\frac{1}{2}$) that combine with one atom of copper. Of course, half an atom does not exist, but for the purposes of this calculation the notion of half an atom is useful. In Cu_2O , therefore, the valency of copper is one.

Evidently copper forms some compounds in which its valency is one and others in which its valency is two. Experiment 3 therefore confirms what we suggested earlier, that the valency of some elements is *not* a fixed quantity. This observation raises certain problems.

It is not possible in general to predict chemical formulae from a knowledge of valency. However, some elements have one dominant valency whereas most other elements have a few (not more than two or three) common values of valency. So it is possible to predict the formulae of a small number of simple binary compounds that might form between two elements. The variability of valency also makes it more difficult to formulate simple theories of chemical combination that can account for all compounds of elements that have more than one valency.

- ☐ From the valencies of copper in compounds that you have investigated, what binary compounds of copper and chlorine would you predict?
- ☒ Copper would be expected to form two compounds with chlorine. First, copper(I) chloride, CuCl , in which copper has a valency of one. This does exist, and is a white powder. Second, copper(II) chloride CuCl_2 , in which its valency is two. This also exists, and is a brown powder.

The copper(II) chloride in your Experiment Kit is blue because it contains copper of valency two, together with water. A dilute solution of copper(II) chloride in water also has a blue colour. This colour is characteristic of solutions of compounds of copper in which its valency is two. For example in Experiment 1, the blue solution of copper chloride that you obtained indicated that the copper that was present had a valency of two.

You should now consider the observations that you recorded in Part 2 of Experiment 3. Deduce from these any evidence that the valency of copper changes in this reaction. It will be helpful to try to identify the products from their appearances and to write a balanced equation to represent the reaction. You should then compare your deductions with those from Part 1, including the representation of the reaction in Part 1 as a chemical equation (SAQ 14).

SAQ 14 Write a balanced chemical equation to represent the reaction that you observed in Part 1 of Experiment 3.

SAQ 15 Lead forms a number of oxides. The formulae of two of these are PbO and PbO₂. What is the valency of lead in each of these compounds?

SUMMARY OF SECTION 3

1 The chemical composition of a chemical compound can be determined by measuring the masses of the elements that combine to produce the compound. The numbers of atoms (or moles) of the elements present in a chemical compound are generally found to be in a ratio of small integers. The composition of a compound is represented by its chemical formula written as chemical symbols with subscripts that indicate the relative numbers of atoms (or moles).

2 The mole is defined as the amount of the isotope ¹²C that has a mass of exactly 12 g. A mole of substance contains approximately 6.022×10^{23} atoms (if an element) or 6.022×10^{23} molecules (if a compound).

3 Chemical reactions are represented by chemical equations. A chemical equation shows the reactants on the left-hand side and the products on the right, with the substances represented by chemical formulae. Chemical equations must be balanced; the same number of atoms of each type of element must appear on both sides of the equation.

4 The valency of an element is equal to the number of hydrogen atoms that combine with one atom of that element. Elements have either a single value or a small number of values of valency. So valencies of an element are useful in the prediction of the formulae of the possible compounds that the element might form.

4 CHEMICAL PERIODICITY

STUDY COMMENT During this Section, you will need the pack of Periodic Table data cards that was mailed with these Units.

You are now ready for an introduction to one of the greatest of all chemical discoveries. In Units 11–12, you met the concept of relative atomic mass; now you have encountered the idea of the chemical formula of a compound. These two concepts can be used to reveal something very important about the chemical elements.

Chemical elements are, in general, very different from one another. For example, the differences between oxygen, carbon, gold and aluminium are obvious and profound. But, as we show in the TV programme 'Elements discovered', *certain* elements are alike. Thus helium, neon and argon are all colourless gases at room temperature, and they form no chemical compounds. They are therefore grouped together in a set called the **noble gases**.

In the TV programme, you watched the preparation of the metal potassium by electrical methods. Such methods must also be used to prepare the metals lithium and sodium. These and other similarities between the elements, lithium, sodium and potassium, are recognized by mentally grouping them together in a family called the **alkali metals**. Finally, you met members of a family called the **halogens**. They are coloured, volatile substances, which have pungent smells and consist of molecules made up of pairs of atoms. For example, the iodine (I₂) that you used in Experiment 2 is a purple solid that is easily vaporized; bromine (Br₂) is a volatile red liquid, and the pale-yellow fluorine (F₂) and greenish-yellow chlorine (Cl₂) are gases at room temperature.

In the next Section, you will find that such similarities follow a pattern. There, you will arrange the chemical elements in order of relative atomic

NORMAL OXIDE

GROUP

PERIOD

PERIODIC LAW

PERIODIC TABLE

MAXIMUM VALENCY

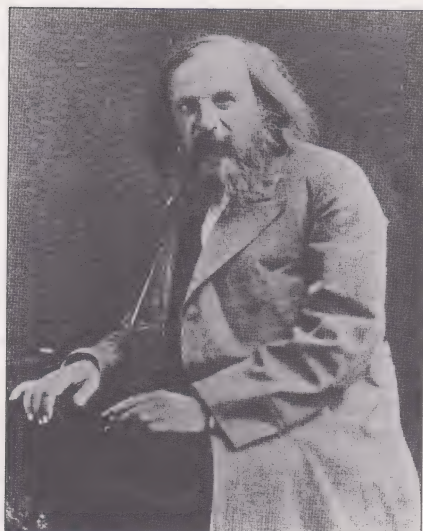


FIGURE 11 Dmitri Mendelée (1834–1907) was a man of fiery temperament and unorthodox appearance. He was remarkable for allowing himself only one haircut a year.

mass. By examining the chemical formulae of the compounds that the elements form, you will find that similar elements turn up at predictable intervals. In 1869, this discovery was used by a Russian chemist, Dmitri Ivanovitch Mendelée (Figure 11), in an especially dramatic way.

4.1 MENDELÉE'S SHORT PERIODIC TABLE

Take your data cards out of their envelope. *Do not open the smaller envelope.* On most of the cards are printed the name and symbol of a chemical element, along with some of its physical and chemical properties, including its relative atomic mass. However, one card is a blank apart from the name and symbol for the hypothetical element scandalum, another is in the smaller envelope, and four of the cards have no relative atomic mass printed on them. Set these six cards on one side. Now, work with the remaining 16 cards. Put them in order of increasing relative atomic mass, and then arrange the eight elements with the smallest relative atomic masses in a row so that relative atomic mass increases from left to right. Examine their properties.

Do you see any trends as you look from left to right?

The arrangement that you should have is

He Li Be B C N O F

There are some obvious trends in the formulae of compounds. The compounds whose formulae are on the cards are the oxides,* hydrides and chlorides of the elements which exist at room temperature. If you write the formulae of the oxides as M_2O_n ,† then from He to B, n takes the values 0, 1, 2 and 3; we use the value zero for helium because it does not form an oxide at all. The next two elements, carbon and nitrogen, form more than one oxide. However, if you pick out the *highest* oxide, the oxide that contains the highest proportion of oxygen, $n = 4$ for carbon and 5 for nitrogen. Thus, the trend that runs from helium to boron continues to nitrogen.

Beyond nitrogen, however, it peters out: F_2O_7 , for example, does not exist.

In the case of hydrides, we can write the formula MH_n . Again if we restrict ourselves to the *highest* hydrides, that is, those that contain the greatest proportion of hydrogen, then right across the row, n follows the sequence 0, 1, 2, 3, 4, 3, 2, 1: the values of n rise in steps of one unit until they reach a maximum value of four, and then fall off in steps of one unit. Finally, the formulae of the highest chlorides follow the same trend as those of the highest hydrides.

These patterns can scarcely be a matter of chance. Now turn to the remaining cards and pick out neon, the element with the next highest relative atomic mass (that is, the next highest above fluorine).

What element in the row before you does this resemble?

Neon, like helium, is a gas, and it forms no compounds of any sort. Register this fact by placing the neon card below the helium card. Now lay out the next seven elements in order of relative atomic mass in this second row.

What trends in the formulae of compounds are visible in this second row?

* By *oxides* in this context, we mean **normal oxides**, a class of compounds such as CuO (Figure 9), in which any oxygen atom is linked only to other types of atom. This excludes compounds called peroxides and superoxides, which contain oxygen atoms linked to one another.

† We choose to write the formula in this way, with n representing the number of atoms of oxygen combining with *two* atoms of M, because we then find that n is always a whole number. Thus, lithium oxide is written Li_2O rather than $LiO_{0.5}$.

The arrangement you should have is

He	Li	Be	B	C	N	O	F
Ne	Na	Mg	Al	Si	P	S	Cl

This time the oxide trend is perfect. When the formulae of the highest oxides are written as M_2O_n , n takes the values 0, 1, 2, 3, 4, 5, 6, 7, from neon to chlorine. The trend in the formulae of the highest hydrides is exactly the same as in the first row, and so is that in the formulae of chlorides, except that at phosphorus, the higher chloride, PCl_5 , is formed. In this kind of arrangement, elements with similar chemical properties (helium and neon; lithium and sodium) fall in vertical columns called **Groups**. The horizontal rows are called **Periods**.

Now take up the four cards with no relative atomic masses printed on them. These all lie in the next Period.

Use their chemical properties to place them in their correct vertical columns, i.e. Groups.

The four elements do not form a continuous sequence within the Period; one element is missing.

In which Group does the missing element lie? Write down the properties you think it might have on the card that refers to the hypothetical element scandalum.

Now open the smaller envelope and compare the observed data with your predictions. If your predictions were anything like correct, you have understood one of the greatest scientific achievements. Like you, Mendeléeve noticed that when the chemical elements were arranged in order of their relative atomic masses, they displayed a periodicity in chemical properties. He called this phenomenon the **Periodic Law**. Others before him had noticed the phenomenon, but the touch of genius that Mendeléeve brought to the problem was the willingness to leave empty spaces in his **Periodic Table**, and the boldness to predict the properties of elements that should have filled them. Like you he did not know of an element that, according to his theory, should fall underneath aluminium and lie between calcium and titanium. He therefore claimed that the element had yet to be discovered, and that he knew what the undiscovered element would be like.

Please leave your card arrangement undisturbed. You will need it again in Section 4.2. The arrangement is the beginnings of Mendeléeve's short Periodic Table, which he put together between 1869 and 1871. A later version of this, which includes refinements added by other chemists, is shown in Figure 12. The relative atomic masses are present-day values, and the colour coding will be explained later. All the Groups are numbered, from zero to eight, and the first two Periods are identical with your first two rows of cards. Now recall the formulae of the highest oxides of the elements on those cards.

Can you guess what property of the elements the Group numbers in Figure 12 were meant to represent?

They were meant to represent the number of oxygen atoms that two atoms of the element are combined with in the highest oxide. For example, elements in Group II, such as calcium and barium, form highest oxides of general formula MO , two oxygen atoms being combined with every two atoms of M . Put another way, they were meant to represent the valencies of the elements in the highest oxides, when valency is defined in the sense introduced in Section 3.3. More generally, since the elements usually display their **maximum valencies** in their highest oxides, the Group numbers were meant to represent the highest valencies of the elements. For Mendeléeve, the maximum valency, and therefore the formula of the highest oxide, was a crucial Periodic property through which an element could be assigned to its correct Group. Thus the highest oxide of carbon is CO_2 , and from Section 3.3 the valency of carbon in CO_2 (its maximum valency) is 4. Therefore, carbon can be placed with some confidence in Group IV.

	Group 0	Group I A B	Group II A B	Group III A B	Group IV A B	Group V A B	Group VI A B	Group VII A B	Group VIII
Period 2	2 He 4.00	3 Li 6.94	4 Be 9.01	5 B 10.8	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	
Period 3	10 Ne 20.2	11 Na 23.0	12 Mg 24.3	13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	
Period 4	18 Ar 39.9	19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 27 Co 28 Ni 55.8 58.9 58.7
		29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	
Period 5	36 Kr 83.8	37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc 98.0	44 Ru 45 Rh 46 Pd 101 103 106
		47 Ag 108	48 Cd 112	49 In 115	50 Sn 119	51 Sb 122	52 Te 128	53 I 127	
Period 6	54 Xe 131	55 Cs 133	56 Ba 137	57–71 *	72 Hf 178	73 Ta 181	74 W 184	75 Re 186	76 Os 77 Ir 78 Pt 190 192 195
		79 Au 197	80 Hg 201	81 Tl 204	82 Pb 207	83 Bi 209	84 Po 209	85 At 210	
Period 7	86 Rn 222	87 Fr 223	88 Ra 226	89 Ac 227	90 Th 232	91 Pa 231	92 U 238		

* Rare earth elements:

57 La 139	58 Ce 140	59 Pr 141	60 Nd 144	61 Pm 147	62 Sm 150	63 Eu 152	64 Gd 157	65 Tb 159	66 Dy 163	67 Ho 165	68 Er 167	69 Tm 169	70 Yb 173	71 Lu 175
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FIGURE 12 A later version of MendeléeV's short Periodic Table. Atomic numbers and relative atomic masses are included for each element; the colour coding is explained in Section 4.4. Notice that hydrogen, which belongs in Period 1, has been omitted. The reason for this is discussed in SAQ 36.

In Figure 12, the missing element of your card exercise carries the symbol Sc. It is now called scandium (not scandalum!). In the early 1870s, MendeléeV realized that this element had yet to be discovered, and he predicted some of its properties. His predictions were similar to, but more extensive than those on your sealed envelope card, and they were startlingly confirmed with the discovery of the element by a Swedish chemist, Lars Nilson, in 1879. MendeléeV also published accurate predictions of the properties of gallium (relative atomic mass 70; discovered 1875) and germanium (relative atomic mass 73; discovered 1886).

Finally two further points about periodic trends: first notice that periodicity in chemical properties is not easily detected. You saw it most plainly when you looked at the formulae of compounds, and even then, you had to choose your compounds quite carefully. For example, you studied the variation in the formulae of the *highest* oxide and ignored lower oxides. Any pattern in the formulae of lower oxides is less obvious, and is ignored in this Course.

Secondly, even when you made these careful choices, the periodic patterns are by no means perfect. You saw this in the first row of cards that you laid out, when the trend in the formulae of the highest oxide petered out at nitrogen. Let us summarize the important trends we have looked at, and at the same time give you some idea of how good they are. There were three of them, and they can be described by referring to Figure 12.

1 If we write the formula of the highest oxide as M_2O_n , then as we move across any horizontal line of the Table from Group 0 to Group VIII, n increases from zero in Group 0 to 8 in Group VIII. This trend works for 74 of the 91 elements in Figure 12. One familiar exception is copper, whose position in Group 1 suggests a highest oxide Cu_2O . In fact, there is a highest oxide CuO , which you made and used in Experiment 1.

2 If we write the formula of the highest hydride as MH_n , then as we move across any horizontal line of the Table from Group 0 to Group VII, n follows the pattern, 0, 1, 2, 3, 4, 3, 2, 1. This time we have left out Group

VIII: the trend works for just over 60 of the 82 elements in Groups 0 to VII of Figure 12.

3 If we write the formula of the highest chloride that is known to exist at room temperature as MCl_n , then the trend in n is the same as for the hydrides, MH_n . This again works for just over 60 of the 82 elements in Groups 0 to VII of Figure 12.

The statistics that we have quoted tell you that periodic patterns in chemical behaviour are by no means perfect. Nevertheless, they are quite good enough to enable you to make reasonably confident predictions about the chemistry of elements that you know nothing about. In any problems in this Course, you may assume that the three trends cited above are perfect.

4.2 A PROBLEM RAISED BY SOME RELATIVE ATOMIC MASSES

Mendeléeev's work was immensely successful, but he also encountered difficulties. One of them can be identified by returning to your array of cards.

The bottom row of your array should contain five elements: Ar, K, Ca, Sc and Ti. Relative atomic masses have not been printed on four of these cards. The values are Ar = 39.9, K = 39.1, Ca = 40.1, and Ti = 47.9.

Write these values on the cards, and then re-examine the entire bottom row. Can you detect any anomalies?

The properties of argon and potassium clearly show that argon is a member of Group 0 and that potassium is a member of Group I. Thus, argon precedes potassium in the Periodic Table. But the relative atomic mass of argon is greater than that of potassium. Here then is one of the problems that Mendeléeev encountered: it was necessary, at one or two points, to depart from the order of relative atomic masses if the periodicity in chemical properties was to be maintained.

Can you solve this problem by using what you have already learnt in earlier Units?

This difficulty can be eliminated by thinking back to Units 11–12. There you found that neon gas consisted of three isotopes, ^{22}Ne , ^{21}Ne and ^{20}Ne . Chemically speaking, the three isotopes of neon behave identically—they are all neon—but they differ in relative atomic mass. Relative atomic masses of naturally occurring elements depend on the isotopic composition of the element and so do not uniquely distinguish one element from another.

- ☐ What property does uniquely distinguish one element from another?
- ☒ Its *atomic number*—the number of protons in the nucleus.

If Mendeléeev's Periodic Law is rephrased to state that the chemical properties of the elements are a periodic function of atomic number, rather than relative atomic mass, the potassium–argon anomaly disappears. The isotopic compositions of natural potassium and natural argon are such that the relative atomic mass of argon exceeds that of potassium, even though the atomic numbers (18 and 19) are in the reverse order. All other anomalies of this sort can be disposed of in a similar way.

Please leave your array of cards undisturbed. You will need it again in Section 4.4.

4.3 A CRITIQUE OF THE SHORT TABLE

You have seen the importance that Mendeléeev placed on periodicity in the formulae of compounds, and especially on periodicity in the formulae of the highest oxides of the elements. However, to bring out this periodicity, the Table shown in Figure 12 had to include several features that seemed con-

RARE EARTH ELEMENT

LONG PERIOD

SUB-GROUPS A AND B

trived. Two of these features are places where more than one element has been crammed into a single space in the Table:

1 Group VIII occurs only in some Periods and in each space it contains three elements instead of one.

2 Even more striking, 15 elements, numbers 57–71 inclusive, all occupy one space in the Table. These are all members of a family called the **rare earth elements**. The symbols, atomic numbers and relative atomic masses for these elements appear in a footnote to the Table. They were nearly all discovered after 1870 and proved a severe embarrassment to proponents of the Mendeléev Table. In particular, they nearly all formed highest oxides with the formula M_2O_3 .

Why was this embarrassing?

If each element were allotted *one* space in the Table, element 57, lanthanum, would fall in Group III; element 58, cerium, in Group IV; element 59, praseodymium, in Group V, and so on. As the highest oxide in most of the 15 cases is M_2O_3 , this would cause a catastrophic disruption in the periodicity in the formulae of highest oxides. For this reason, only one space was allotted to the 15 elements.

3 At the head of each Group are printed the letters A and B. These symbols only take on meaning in the fourth Period where the so-called **long Periods** begin. The long Periods, Periods 4, 5 and 6, start with a noble gas in Group 0 and complete their first crossing of the Table with a Group VIII 'threesome'. But they do not finish there. They now make a second crossing, beginning in Group I with copper (Cu), silver (Ag) and gold (Au), respectively. In Groups I to VII, the elements of the first crossing of the long Periods are placed in the A column and are said to belong to **sub-Group A**. The elements of the second crossing are placed in the B column, and are said to belong to **sub-Group B**. This division was necessary because, although there was some resemblance between the chemistry of the elements of sub-Group A and those of sub-Group B, it was not nearly as close as the similarities within each sub-Group. For example, copper, silver and gold, the elements of Group IB, can be used to make coins because they undergo little or no reaction with air or water. By contrast, as you will see in the TV programme 'Elements organized', the alkali metals (Group IA) react violently in air or water, and may even explode.

4.4 THE TRANSITION TO THE LONG FORM OF THE PERIODIC TABLE

We have just described some of the contrived characteristics of Figure 12. Can these be eliminated?

You know that the form of Mendeléev's Table was dictated by the need to preserve the periodicity in the formulae of compounds, and especially in the formulae of the highest oxides. In a redesigned form in which the contrived features have been eliminated, this periodicity may have to disappear. If so, it is important that, as compensation, the revised Periodic Table should forcefully bring out new periodicities that were obscured in Figure 12.

To illustrate this, we shall examine which elements are metals, and which are not. Look again at Figure 12. In this Table, metals* are shaded red, non-metals* are shaded grey and semi-metals* are shaded pink. Obviously Mendeléev's short Table does not create a simple pattern out of these three classes. Thus non-metals occur on both the left and right sides of the Table, with metals and semi-metals in between.

* The fuller meaning of these terms is explained later. Here it is enough to have some idea of what a metal is!

- ☐ Which non-metals occur on the left-hand side of the Table?
- The noble gases (He, Ne, Ar, Kr, Xe and Rn).

This left-side position of the noble gases will hinder any attempt to bring order to the distribution of our three classes. Let us see if we can eliminate it by returning to your array of cards. You are told on these cards whether an element is a metal, semi-metal or non-metal. As in Figure 12, the noble gases (He, Ne and Ar) occur in a column at the beginning of the rows of your array. Now suppose this noble gas column is blanked out.

- ☐ Do you see any pattern in the distribution of metals, semi-metals and non-metals within the remaining parts of each row of cards?
- Each row now begins with a metal (Li, Na, K). As we move across the completed rows, which now begin with lithium and sodium, metals are succeeded first by semi-metals, and then by non-metals.

What we want you to do is to move the three noble gas cards so that they, too, fit into this pattern. But remember that your new arrangement has to be a Periodic Table. This will be so if two conditions are fulfilled:

- 1 As before, the elements must appear in order of atomic number.
- 2 Elements that were in vertical columns before your rearrangement are in vertical columns afterwards.

- ☐ Can you see how to do it?
- Move each noble gas to the end of the *preceding* row.

Your arrangement should now be:

							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti				

As required, in the two completed rows, metals now appear on the left, non-metals on the right, and semi-metals in between.

A rather similar trick can be pulled at other points in Figure 12 where our metals/left, non-metals/right condition is not met. Look at Period 4 of Figure 12. This is a doubled long Period, and after each noble gas has been moved to the end of the preceding Period, it begins with potassium, and ends with bromine and the noble gas, krypton. At this stage, the elements of the first crossing, K to Ni, are all metals; only in the second crossing, Cu to Kr, does the metals/left, non-metals/right condition materialize.

But what happens if the second crossing is stuck on the end of the first by joining copper to nickel?

The result is as follows:

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
---	----	----	----	---	----	----	----	----	----	----	----	----	----	----	----	----	----

The metals/left, non-metals/right condition is now fulfilled throughout the Period. In Figure 13, the same change has also been made to other long Periods. Notice that this procedure results in rows of obviously unequal length. To ensure that elements in the A and B columns of Figure 12 remain in columns in Figure 13, the rows beginning with Li, Na, K and Rb have been pulled apart after their Group II elements Be, Mg, Ca and Sr. Such a manoeuvre does not just keep elements in their proper columns; it also allows us to fit the rare earth elements into the pattern *within the main body of the Table*.

In Figure 13, the contrived features of Figure 12 have now disappeared. In this 'long form' of the Periodic Table, all Periods begin with metals. Across each Period, metals give way first to semi-metals, and then to non-metals.

FIGURE 13 A rearrangement of Figure 12 to a long form of the Periodic Table, which brings out the pattern in the distribution of metals (red), semi-metals (pink) and non-metals (grey).

metals																semi-metals				non-metals													
3 Li	4 Be															5 B	6 C	7 N	8 O	9 F	10 Ne			2 He									
11 Na	12 Mg															13 Al	14 Si	15 P	16 S	17 Cl	18 Ar												
19 K	20 Ca															21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn			31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr															39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd			49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg			81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U																												



FIGURE 14 Alfred Werner (1866–1919). Born in Alsace, he later took Swiss nationality and worked in Zurich. In 1905, he published an essentially modern Periodic Table, and in 1913 was awarded a Nobel Prize for work on transition metal chemistry. A sociable man, he liked billiards, cards and drink. The latter probably contributed to an early death from arteriosclerosis.

The Group VIII ‘threesomes’ and the A and B sub-Groups have been swept away, and the rare earth elements are laid out horizontally in full. By using arguments not too dissimilar from ours, a Table like this was arrived at in 1905 by a German chemist, Alfred Werner (Figure 14). In Section 5, we shall use the electronic configurations of atoms, which you studied in Units 11–12, to show that such Tables are more fundamental than that in Figure 12.

You have now finished with your data cards.

SUMMARY OF SECTION 4

1 Between 1869 and 1871, Mendeléeiev showed that the chemical properties of the elements are a periodic function of relative atomic mass. This periodicity is strongly apparent in the formulae of compounds, especially those of the highest oxides. Mendeléeiev’s discovery enabled him to predict the properties of undiscovered elements.

2 One weakness of Mendeléeiev’s system was the need to depart from the order of relative atomic masses at some points to preserve periodicity. This defect was eliminated by arranging the elements in order of atomic number. Other weaknesses included contrivances that were necessary to preserve the periodicity in the formulae of compounds. Among these were the A and B sub-Groups, and the placing of the Group VIII and rare earth elements in single spaces in the Table.

3 If the Periodic Table is reconstructed to show periodicity in the distribution of metals, semi-metals and non-metals, the contrived features of Mendeléeiev’s Table disappear.

SAQ 16 An element X of the third Period falls in Group III. An element Y of the sixth Period falls in sub-Group A of Group V. Use Figure 12 to identify X and Y.

SAQ 17 An element M forms a chloride MCl_4 and a single oxide MO_2 . Which two of the following elements could it possibly be? (a) Strontium (Sr, atomic number 38); (b) ruthenium (Ru, atomic number 44); (c) actinium (Ac, atomic number 89); (d) hafnium (Hf, atomic number 72); (e) tin (Sn, atomic number 50); (f) tungsten (W, atomic number 74).

SAQ 18 An element Z is a semi-metal, and forms two oxides, Z_2O_3 and Z_2O_5 , and a single hydride, ZH_3 . Its relative atomic mass lies between 80 and 130. Identify the element, and state the Group and Period of the Periodic Table in which it lies.

5 ELECTRONIC STRUCTURE AND THE PERIODIC TABLE

We now have two kinds of Periodic Table competing for survival. Both have something to offer. Important patterns in the formulae of compounds are represented quite simply in Mendeléeiev’s short Table. The long form does not do this so well, but it is free of the contrived features of the Mendeléeiev Table, and it brings out the periodic distribution of metals, semi-metals and non-metals.

What we shall do is to subject both Tables to further tests, by looking at another property of the chemical elements that shows periodicity. If one of the two Tables represents the periodicity in that property more clearly than the other, we shall have an additional reason for preferring it. The property that we have chosen is the electronic structure of atoms in the ground state, which you met in Units 11–12. We begin therefore by revising what you have already learnt about this topic.

5.1 REVISING ELECTRONIC CONFIGURATIONS

In Units 11–12 you were shown how to assign an electronic configuration to an atom, given its atomic number and an energy-level diagram. The following questions give you a chance to revise this procedure.

The electrons in an atom are arranged around the nucleus in a series of shells. Each shell is specified by a single quantum number, the principal quantum number.

- ☐ What symbol is used for the principal quantum number, and what values can it take?
- The principal quantum number is given the symbol n , and n can take the values 1, 2, 3, 4, 5, etc.

The electrons in any shell are grouped into a series of subshells. Each subshell is specified by a second quantum number, l .

- ☐ How many subshells are there in a shell of principal quantum number 4? Assign an l value to each subshell.
- For a shell of principal quantum number n , l can take values from zero up to $(n - 1)$. Thus, in the shell for which $n = 4$, there are subshells with the values $l = 0, 1, 2$ and 3.

An alternative way of specifying subshells uses letters in place of the quantum number l . The following letters are used in this other notation:

s for subshells with $l = 0$
 p for subshells with $l = 1$
 d for subshells with $l = 2$
 f for subshells with $l = 3$

Thus, the four subshells in the shell for which $n = 4$ are written 4s, 4p, 4d and 4f.

In Units 11–12, you met two further quantum numbers, which together specify individual electrons within each subshell. However, these extra quantum numbers will not be needed here. All you need to know is that there is an *upper limit* on the number of electrons that each kind of subshell can hold.

- ☐ What is this upper limit for s, p, d and f subshells?
- For s, p, d and f subshells, the upper limits are 2, 6, 10 and 14 electrons, respectively.

To assign electronic configurations to atoms you only need one more piece of information. *This is a diagram displaying the subshells in order of ascending energy.* Surprisingly enough, electronic configurations can be correctly assigned to *nearly all* atoms using just one such diagram, Figure 15. In assigning configurations, you fill the subshells in order of ascending energy, moving on to the subshell of next highest energy when any subshell becomes full. Figure 16, which you may remember as Figure 47 in Units 11–12, also shows the order in which the subshells fill. It is easily obtained from Figure 15.

- ☐ The atomic number of silicon is 14. Write down the electronic configuration of the silicon atom.
- $1s^2 2s^2 2p^6 3s^2 3p^2$. Assign the 14 electrons in the silicon atom to the energy-level diagram. The 1s and 2s levels on the left of Figure 16 each take two electrons. The next highest level is 2p and this subshell is filled by the next six electrons. The 3s subshell then takes another two electrons and the thirteenth and fourteenth electrons go into the subshell of next highest energy, which is 3p.

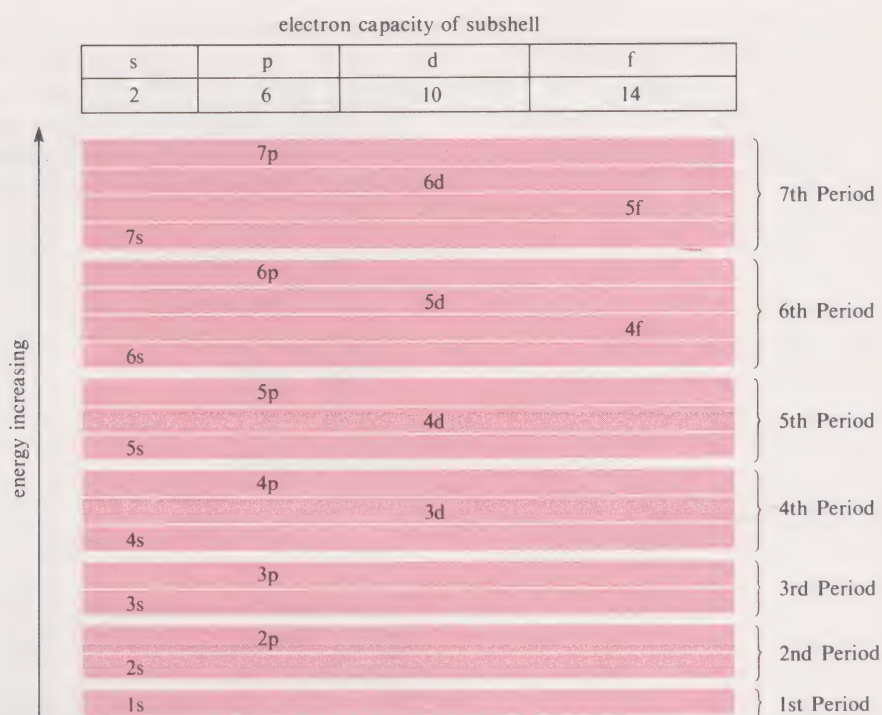


FIGURE 15 Subshell energy level diagram.



FIGURE 16 Order of ascending energy for the subshells.

5.2 THE PERIODICITY IN ELECTRONIC CONFIGURATION

We shall now show you that as we move from element to element in order of increasing atomic number, the electronic configurations of the atoms show a *periodic variation*. You will see that this periodicity is better described by the long form of the Table than by Mendelée'v's system. While reading this Section, you may find it useful to refer to the Table of electronic configurations in Appendix 2 of Units 11-12.

Let us start with Figure 13. We shall ignore the first Period in Figure 13 for the moment and write out the second Period. This is

3	4	5	6	7	8	9	10
Li	Be	B	C	N	O	F	Ne

MAIN GROUP ELEMENTS

TYPICAL ELEMENTS

TRANSITION ELEMENTS

The lithium atom has the configuration $1s^22s^1$. In beryllium the 2s level contains a second electron and is full; the configuration is $1s^22s^2$. The next highest energy level is 2p, so the electronic configuration of boron is $1s^22s^22p^1$. From boron to neon, successive electrons are added to the 2p level, until at neon the configuration is $1s^22s^22p^6$. The electronic configurations of the elements from lithium to neon are as follows:

Li	$1s^22s^1$
Be	$1s^22s^2$
B	$1s^22s^22p^1$
C	$1s^22s^22p^2$
N	$1s^22s^22p^3$
O	$1s^22s^22p^4$
F	$1s^22s^22p^5$
Ne	$1s^22s^22p^6$

The element after neon is sodium.

- ☐ Is the electronic configuration of sodium $1s^22s^22p^7$?
- ☒ No. At neon, the 2p level is full—it can accommodate only six electrons.

From Figure 16, the next highest energy level is 3s so the configuration of sodium is $1s^22s^22p^63s^1$. For the eight elements after neon, you should fill the 3s and 3p levels in the way that you filled the 2s and 2p levels across the second Period. You can therefore group the two rows as follows:

Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

- ☐ What common feature is shared by the electronic configurations of elements in the same column?
- ☒ Their *outer* electronic configurations are the same. For example, for both carbon and silicon, the occupied level of highest energy is a p subshell and in both cases it contains two electrons.

Now let us pause to summarize what we are doing. The electronic configuration of atoms is a periodic property because when we lay out the elements in order of atomic numbers, elements whose atoms have similar outer electronic configurations, such as carbon and silicon, occur at intervals. By grouping such elements in columns, we are constructing a Periodic Table that represents the periodicity in electronic configuration.

The elements in the two rows that we have laid out have outer electronic configurations of the type ns^1 , ns^2 , and ns^2np^1 to ns^2np^6 . Such elements are called **typical** or **main group elements**.

You should now be able to see that the members of certain families of elements with which you are already familiar have similar outer electronic configurations and are included among the typical elements. Thus, the alkali metals, which include lithium and sodium, have outer electronic configurations of the type ns^1 . Again, the noble gases, with the exception of helium, have outer electronic configurations of the type ns^2np^6 .

- ☐ The two elements after argon are potassium and calcium. Are these typical elements?
- ☒ Yes. They have outer electronic configurations $4s^1$ and $4s^2$, respectively. Potassium can be grouped under sodium, and calcium under magnesium.
- ☐ The next element is scandium. Is this a typical element?

- No. Figures 15 and 16 show that when the 4s level is full, the 3d level begins filling rather than the 4p.

If we write out the subshells in the order of increasing energy given by Figures 15 and 16, then the electronic configuration of scandium is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$. The 4p level only begins filling at gallium (element 31), when the 3d level has been filled. *Typical elements thus reappear at gallium. The elements between calcium and gallium span the region in which the 3d shell is filling up.* There are ten of them, because the 3d level can accommodate up to ten electrons. As their configurations are of this type, they cannot be grouped under typical elements, so the block of typical elements is usually pulled apart between calcium and gallium, and the ten elements are inserted there:

3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr

The elements scandium to zinc are called **transition elements** because they form a bridge between two blocks of typical elements. We define transition elements as the elements that span a region in which a d shell is filling. In the scandium to zinc series their most common outer electronic configuration is of the type $4s^2 3d^x$, where x runs from 1 to 10.

As you may recall from Units 11–12, two of these ten transition elements, chromium and copper, do not have outer electronic configurations of the type $4s^2 3d^x$. Their outer electronic configurations are $4s^1 3d^5$ and $4s^1 3d^{10}$. These exceptions are a reflection of the fact that, in the scandium to zinc region, the 3d and 4s energy levels are fairly close in energy. Nevertheless, the remaining eight transition elements of this row do have outer electronic configurations of the type $4s^2 3d^x$.

The grouping in the array above has set the transition elements apart from the typical elements, and there is experimental support for this: the transition elements have properties different from those of the typical elements. Among the characteristics of transition elements are the following:

- They are *all* metals (see Figure 13);
- Their compounds are often strongly coloured;
- They often form more than one compound with other elements. In particular, they often form two or more halides with the formula type MX_n (where X represents a particular halogen element) and two or more oxides with the formula type M_2O_n . In such cases the values of n usually differ by one. Thus iron forms a dichloride $FeCl_2$, and a trichloride $FeCl_3$, which are pale green and yellow-brown, respectively. Chromium forms the following fluorides: CrF_2 , CrF_3 , CrF_4 , CrF_5 and CrF_6 , and copper, as you showed in Experiment 3, yields the oxides Cu_2O and CuO . By contrast, typical elements form two or more chlorides or oxides less often, and when they do the values of n usually differ by two. Thus lead forms just two chlorides, $PbCl_2$ and $PbCl_4$.

Now let's get back to electronic configuration: after the series of transition elements has been completed, the 4p level begins filling at gallium. When the 4p level becomes full at the noble gas krypton, the fourth Period ends.

On to the fifth Period: with regard to electronic configuration, this is a straightforward repeat of the fourth.

What energy levels are filled in the fifth Period?

From Figures 15 and 16 you can see that the 5s level is filled first (rubidium and strontium). Then the filling of the 4d level generates a second series of transition elements, from yttrium to cadmium:

3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe

Typical elements reappear with the filling of the 5p level at indium, and the Period ends when the 5p level is full at the noble gas xenon.

LANTHANIDES

5.3 THE SIXTH PERIOD

The sixth Period begins with the elements caesium and barium. If we represent the electronic configuration of the noble gas, xenon, by the symbol [Xe], then the electronic configurations of caesium and barium are $[\text{Xe}]6s^1$ and $[\text{Xe}]6s^2$, respectively. The atomic number of barium is 56. Refer again to the energy-level diagrams, Figures 15 and 16. Use them to predict the electronic configurations of the following elements: lanthanum (atomic number 57), praseodymium (59), terbium (65), ytterbium (70), lutetium (71).

The two Figures show that after 6s the level of next highest energy is 4f, followed by 5d. The 4f level can accommodate up to 14 electrons. The procedure we have been following therefore suggests the following configurations: lanthanum, $[\text{Xe}]6s^2 4f^1$; praseodymium, $[\text{Xe}]6s^2 4f^3$; terbium, $[\text{Xe}]6s^2 4f^9$; ytterbium, $[\text{Xe}]6s^2 4f^{14}$ and lutetium, $[\text{Xe}]6s^2 4f^{14} 5d^1$.

With one exception* these predictions are correct. They suggest that after barium, a new series of elements appears in which the 4f shell is being filled.

- ☐ How many elements will there be in this new series?
- ☒ There must be 14 because f shells can accommodate 14 electrons.
- ☐ At what element does the 4f shell become full?
- ☒ At ytterbium, which has the configuration $[\text{Xe}]6s^2 4f^{14}$.

We shall therefore define the new series as the 14 elements from lanthanum to ytterbium, inclusive. These 14 elements, which follow barium, are called **lanthanides**. Their most common electronic configuration is of the type $[\text{Xe}]6s^2 4f^x$. In general then, we can say that the lanthanides are typified by the outer electronic configuration $6s^2 4f^x$, where x runs from 1 to 14. Because they cannot be grouped beneath elements that we have considered up until now, we must pull the Periodic Table apart again, and insert them after barium as in Figure 17. After the 4f level has been filled at ytterbium, lutetium, which has the configuration $[\text{Xe}]6s^2 4f^{14} 5d^1$, begins a new series of transition elements.

* There is one flaw in the definition of the lanthanide elements used in this Unit: lanthanum, which is predicted by the use of Figures 15 and 16 to have the configuration $[\text{Xe}]6s^2 4f^1$, does in fact have the configuration $[\text{Xe}]6s^2 5d^1$. Now the definition of the lanthanides that we have given above makes lanthanum the first lanthanide, so we must face the ironic fact that our first lanthanide does not contain a 4f electron. Again, the problem arises because two energy levels, 4f and 5d, are rather close in energy. As Figures 15 and 16 lead us to correct lanthanide configurations in nearly all cases, we can regard the electronic configuration of lanthanum as an anomalous case similar to those of chromium and copper, which were mentioned in Section 5.2.

FIGURE 17 The long form of the Periodic Table.

[illegible]

ACTINIDES

You have already seen, in Section 4.3, that Mendelée's Table had no logical place for the rare earth elements. The failure was so striking that one or two chemists even claimed that Mendelée's ideas were worthless. Here, the rare earth elements of Figure 12 have become lanthanides, and they fit as naturally into Figure 17 as do the transition elements. The lanthanides behave very similarly in many chemical reactions, so similarly that only since 1945 has it become possible to separate them completely from each other and obtain pure samples of each. For nearly all of them, the highest oxide has the formula M_2O_3 , and for all 14, the highest chloride is MCl_3 . Recent research has shown that they are ingredients of many of the new superconducting materials that may one day have many important applications. When cooled to low temperatures, superconducting substances conduct electricity without resistance; for these new materials, the required degree of cooling is both less severe, and much less expensive.

As we have already stated, after the 4f level has been filled at ytterbium, stepwise occupation of the 5d shell begins at the next element, lutetium, which has the configuration $[Xe]6s^2 4f^{14} 5d^1$. Lutetium thus begins a new series of transition elements. The new transition series is completed with element number 80, mercury, and more typical elements then appear as the 6p level begins to fill. When the 6p level is filled at the noble gas radon, the sixth Period is complete. The seventh Period then begins as usual with an alkali metal, francium, and a Group II metal, radium, as the 7s level is filled.

5.4 GENERAL COMMENTS ON SECTIONS 5 TO 5.3

Pause here for a moment to consider what has been achieved. By now you should appreciate that the periodicity in the electronic structures of atoms is almost perfectly represented by the long form of the Periodic Table shown in Figure 17 and bears no straightforward relationship to the Mendelée's Table. This is the strongest argument that you have met so far for the superiority of the long form of the Periodic Table.

Moreover, the electronic configurations do not just suggest that the long form of the Table is superior: they also help us to understand the peculiarities of Mendelée's Table. Consider, for example, the A and B sub-Groups. The elements in A sub-Groups have the same *number* of outer electrons as the elements of the B sub-Groups, but the *type* of outer electron configuration is different. Thus, in Group IV of Figure 12, the atoms of Group IVA (titanium, zirconium and hafnium) have outer electronic configurations of the type $ns^2(n-1)d^2$, whereas those of Group IVB (carbon, silicon, germanium, tin and lead) have outer electronic configurations of the type ns^2np^2 . Here, the similarity between an A and a B sub-Group element is related to the fact that both atoms have four outer electrons. But such similarities are not as close as those that exist within the sub-Groups themselves, where not just the *number*, but the *type of configuration* of the outer electrons is similar.

Finally, throughout Section 5, we have relied on the rules of Units 11–12 for building up electronic configurations. The long form of the Table then follows from these rules in a straightforward way. Historically, the problem was the reverse of this: the rules had to be guessed by squaring them with the chemical observations embodied in the Periodic Tables of chemists like Werner. It was for a largely successful exercise of this sort that Niels Bohr (Figure 18) won the 1922 Nobel Prize for Physics. Thus, Periodic Tables were not just a great discovery in their own right; they also played a central role in the solution of one of the most fundamental of scientific problems: the nature of atomic structure.

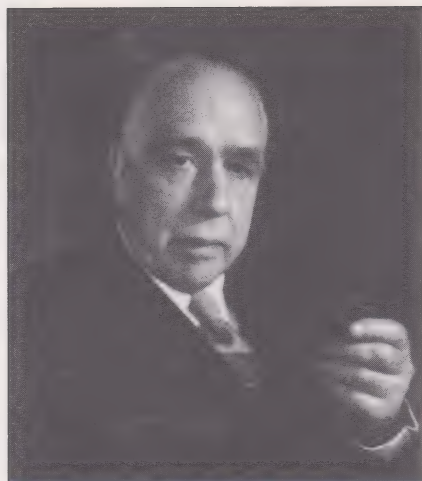


FIGURE 18 Niels Bohr (1885–1962). As a physicist and a philosopher, he had a profound influence upon the development of quantum theory; as a goalkeeper, he narrowly missed selection for the Danish football team in the 1908 Olympic Games. He once said of himself that he ‘lacked the gift of impertinence’, and this may explain why his wartime political meetings with Winston Churchill were not a success. In 1922, he won the Nobel Prize for physics by using the Periodic Table to work out electronic configurations for the atoms of the chemical elements.

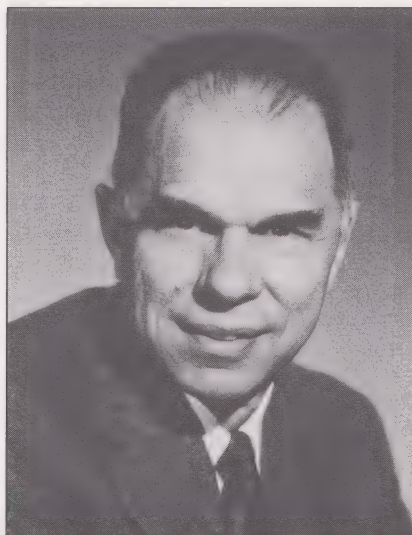


FIGURE 19 Glenn Seaborg. Born in 1912, he led teams which discovered plutonium in 1941, and later, the eight subsequent artificial elements in the Periodic Table. These discoveries were facilitated by his recognition that the elements were members of what he called the actinide series. The work won him a Nobel Prize for chemistry in 1951. His university address can be worked out from the names of three of the elements that he discovered: berkelium, californium and americium.

5.5 THE SEVENTH PERIOD AND BEYOND

Let us now take up the Periodic Table again where we left off. In Section 5.3, you saw that the seventh Period begins with the elements francium and radium (element 88). In Figure 17, the elements beyond this point are classified with the lanthanide elements. This similarity of the elements beyond radium to the lanthanides only became obvious during the wartime programme for the manufacture of atomic bombs in the United States, when teams of scientists under the direction of Glenn Seaborg (Figure 19) succeeded in making new elements with atomic numbers greater than that of uranium. Among these elements is element number 94, plutonium, which can be made by neutron bombardment of uranium in a nuclear reactor.

At a certain point beyond uranium, marked by atomic numbers 95 and 96 (americium and curium), it was found that the elements began to behave like lanthanides. Thus, americium and the elements immediately following it all form a highest chloride of formula MCl_3 . Confronted by this analogy with the lanthanides, Seaborg proposed in 1945 that actinium, and the 13 elements following it, spanned a region in which the 5f level is filling. Notice that this is consistent with Figure 16. These 14 elements are therefore grouped beneath the lanthanides in Figure 17; they are called the **actinides**. Further confirmation of this idea has come with the preparation of elements 104–107. These were made by Soviet and American scientists between 1968 and 1976. Although their names have not been finalized, these elements behave like transition elements rather than like actinides or lanthanides. This suggests that the 5f level is full at nobelium, element 102, and that stepwise filling of the 6d level begins at element 103, lawrencium (see Figure 16).

Beyond uranium, the half-lives of the isotopes of new elements get shorter. Thus, for element 107 the longest-lived isotope known at present has a half-life of only 0.0025 s. However, it is believed that longer-lived isotopes may reappear at certain 'islands of stability' in the region of element 114 and, possibly, elements 126 and 164. Attempts have been made to make or find isotopes of these unknown elements but so far without success.

SUMMARY OF SECTION 5

- 1 The periodicity in outer electronic configuration is best expressed by the long form of the Periodic Table.
- 2 The typical or main-group elements have outer electronic configurations of the type s^x , where $x = 1$ or 2 , or s^2p^x , where x runs from 1 to 6 .
- 3 The transition elements are those series of ten elements that span a region of the Periodic Table in which a d shell is filling.
- 4 The lanthanide and actinide elements are the two series of 14 elements that span the regions of the Periodic Table in which the 4f and 5f levels, respectively, are filling.

Finally, please note one important point. You saw in Section 5 that in the long form of the Periodic Table, the A and B sub-Groups in Mendelée's Table are disentangled. However, Figure 17 shows that Group numbers are retained for Groups IA, IIA, IIIB, IVB, VB, VIB, VIIB and 0 in our new form of the Table: in the long form these drop their suffixes and become the eight main Groups of the long form, the typical elements.

SAQ 19 Use Figures 15 and 16 to work out the electronic configurations of elements 16 and 28. Are these elements typical elements, transition elements, lanthanides or actinides? In what Group of the Periodic Table does element 16 fall? What are the names of the two elements?

SAQ 20 An element M forms solid fluorides MF_2 , MF_3 , MF_4 and MF_5 , their colours being blue, yellow-green, lime-green and colourless, respectively. It forms oxides M_2O_3 , MO_2 and M_2O_5 , their colours being black, dark blue and orange, respectively. Its relative atomic mass is lower than 80. Using Figures 12 and 17, identify the element. Write out its electronic configuration.

SAQ 21 Radon, element 86, marks the point in Figure 16 where the 6p level has become full. Use Figure 16 to predict the electronic configurations of the unknown elements 110, 114, 118 and 119. (Use the symbol [Rn] for the electronic configuration of element 86.) Which, if any, of these four elements is (a) a typical element; (b) a transition element; (c) an alkali metal; (d) a noble gas; (e) an actinide?

6 TWELVE CHEMICAL SUBSTANCES

In these two Units you have been introduced to chemical formulae, which tell you the ratios in which the different kinds of atom combine to form chemical compounds. Carefully chosen examples of these compounds have been combined with the electronic configurations of atoms to demonstrate chemical periodicity, and to build up the long Periodic Table in Figure 17. But how are the atoms held together in the compounds, and why do they combine in one ratio rather than another?

To get the answers to these questions, you must first learn more about some important chemical substances. Sections 6 and 7 supply you with this background information by studying twelve such substances. As the information on them builds up, you will find that it can be organized by using the Periodic Table. The twelve substances are listed in Table 3, and Figure 20 shows the positions of their constituent elements in the Periodic Table.

Four of the substances, NaCl, NaBr, KI and Na₂SO₄, are compounds of the Group I elements sodium and potassium from the extreme left of the Table. Three of these alkali metal compounds also contain Group VII halogen elements, chlorine, bromine and iodine, from the extreme right of the table. Another three of the twelve substances, chlorine, bromine and

TABLE 3 The twelve substances studied in Sections 6 and 7

sodium chloride (NaCl; table salt)	magnesium chloride (MgCl ₂)
sodium bromide (NaBr)	copper(II) chloride (CuCl ₂)
potassium iodide (KI)	water (H ₂ O)
sodium sulphate (Na ₂ SO ₄)	heptane (C ₇ H ₁₆)
chlorine (Cl ₂)	table sugar*
bromine (Br ₂)	
iodine (I ₂)	

* We have omitted the molecular formula because it is terrifying! All you need to know here is that the substance contains carbon, hydrogen and oxygen.

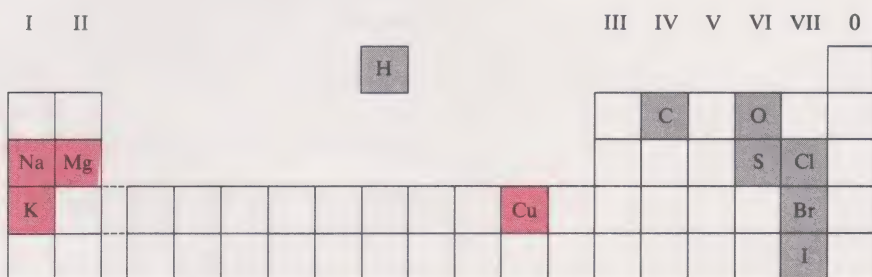


FIGURE 20 A fragment of the Periodic Table of Figure 17 showing the positions of the chemical elements in our twelve chosen chemical substances.

iodine, are elements—the halogens themselves; then there are chlorides of a Group II element, magnesium (MgCl_2), and of a transition element, copper (CuCl_2).

Finally there are three compounds formed from just non-metallic elements from the right-hand side of the Periodic Table. The first is water, H_2O . The other two are heptane and table sugar, which are composed of carbon and hydrogen, and of carbon, hydrogen and oxygen, respectively.

Your study of the twelve substances in Table 3 will provide reasons for classifying the twelve into two distinct sets. Then, in Section 7, you will see that these two sets reflect two different ways in which atoms can be held together in chemical compounds. But learning about these substances will not be an entirely sedentary process. Some of the information will come from two experiments, the first of which follows almost immediately. It is concerned with the electrical properties of liquids and solutions.

6.1 AQUEOUS SOLUTIONS AND THEIR ELECTRICAL CONDUCTIVITY

Everybody knows that two of the twelve substances, salt and sugar, dissolve in a third, water. When this happens, we say that the crystals are *soluble* in water, and that a **solution** has been formed. In these particular cases, it is an **aqueous solution** (from the Latin *aqua*, meaning water) because the **solvent**, the substance in which the crystals, the **solute**, have dissolved, is water. By studying the ability of aqueous solutions to conduct an electric current, you will be led towards a classification of the twelve substances into two important sets.

A crude apparatus for testing the conductivity of a *metal* is shown in Figure 21. It consists of a battery with wire leads attached to its positive and negative terminals. The ends of the wire leads are attached to graphite rods and one of the leads is wired through an electric light bulb. If the ends of the

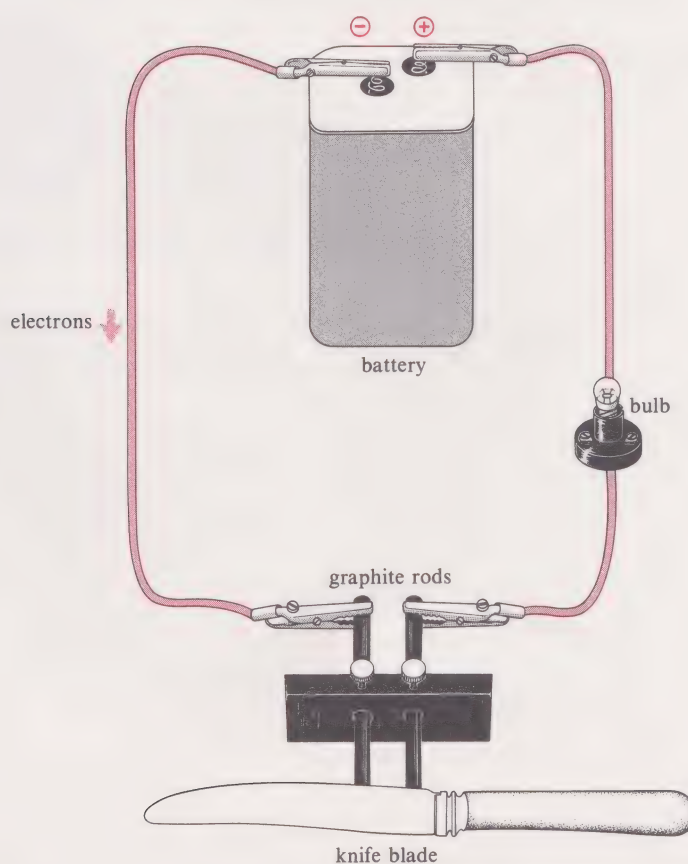


FIGURE 21 Testing the conductivity of a metal.

graphite rods are pressed against the two ends of a metal knife blade, the bulb lights up. This light is produced by the passage of an electric current, that is, the flow of negatively charged electrons, through the filament of the bulb, and this occurs only when the circuit is completed by an electrical conductor.

Thus, the metallic blade, which allows the passage of electrons, is such a conductor, and when it is used to complete the circuit, electrons flow from the negative terminal of the battery, through the graphite rods, blade, bulb filament, and wire to the positive terminal of the battery.

We can find out whether a liquid or a solution conducts electricity by substituting it for the knife blade, as shown in Figure 22. In Experiment 4, you will be doing this, first with distilled water, and then with aqueous solutions of some of our twelve substances. Note that the circuit in Figure 22 is used again in Experiment 5 on page 54; to save time, you are advised to complete this experiment at the same time, but if you wish to do it in its proper place, this will be perfectly acceptable.

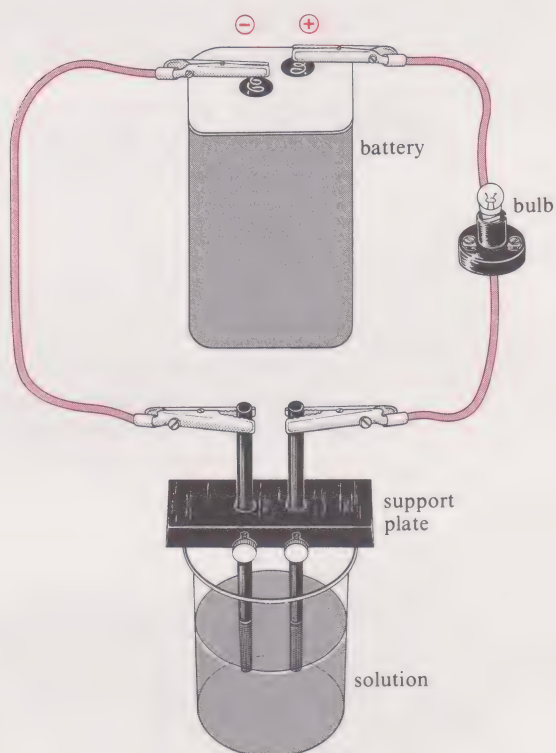


FIGURE 22 Testing the conductivity of a solution.

EXPERIMENT 4 CONDUCTIVITY AND ELECTROLYSIS

TIME

about 45 minutes

NON-KIT ITEMS

distilled water
knife
small screwdriver
a nine-volt battery (for example, a PP7)
white sugar
tissue paper

KIT ITEMS

Chemical tray
copper(II) chloride
dilute hydrochloric acid
(2.4 mol l^{-1})
magnesium chloride
sodium chloride (table salt)
sodium sulphate
Tray A
bulb and holder
glass stirring rod
graphite rods
Tray B
beaker, 100 cm^3
Tray C
crocodile clips (four)
measuring spoon (spatula-type)
pieces of insulated wire (three)
support plate for graphite rods

PART 1

Set up the apparatus as shown in Figure 21. You should be using a nine-volt battery. Touch the knife blade for a fraction of a second across the end of the graphite rods to check that the circuit is complete. (This means that the bulb will light up.)

PART 2

Fill the 100 cm^3 beaker about half full of distilled water and see if the bulb lights up when you set up the arrangement shown in Figure 22.

PART 3

Now remove the graphite rods from the beaker, and add to the water in the beaker about one 'spoon' of sodium chloride. Stir with the glass rod, and when the salt has dissolved, test the solution as in Figure 22 for about 30 seconds. Periodically smell the air inside the beaker during the test. Note down what you smell. Copy Table 4 into your Notebook, and record your observations.

When you have finished, pour the solution away, and rinse the graphite rods and beaker with tap water.

TABLE 4 Observations of electrolysis experiments

Substance	Bulb lights or not?	Smell	What happens at the electrodes?
sodium chloride			
sugar			
magnesium chloride			
sodium sulphate			
copper(II) chloride			

PART 4

Now half fill the beaker with distilled water and repeat the procedure of Part 3, but instead of table salt use sugar. Repeat twice more using first magnesium chloride (MgCl_2) and then sodium sulphate (Na_2SO_4). Fill in the appropriate parts of Table 4.

PART 5

Repeat Part 3 of the experiment, but instead of one 'spoon' of table salt, use two 'spoons' of copper(II) chloride, and test the solution for about $1\frac{1}{2}$ minutes. If at any stage the solution turns cloudy, add one or two drops of hydrochloric acid to clear it. What happens at the graphite rods? Examine the rods at the end of the experiment, note their appearance, and then rinse and clean them up as well as you can with tissue. Record your observations in Table 4.

We now consider the results of these experiments, starting with the tests on water, and on the solutions of sugar and copper(II) chloride.

ELECTROLYSIS

ELECTRODE

ELECTROLYTE

NON-ELECTROLYTE

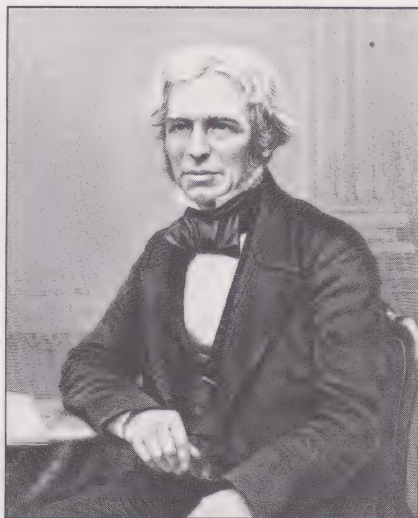


FIGURE 23 Michael Faraday (1791–1867). The son of an English blacksmith, at fourteen he became an apprentice bookbinder. While binding the Encyclopaedia Britannica, he became absorbed in an article on electricity, and put together an electrical generator from old bottles and waste lumber. Subsequently, he invented the electric motor and the dynamo, the bases of electrical power generation, and made fundamental contributions to electrochemistry.

6.2 COPPER(II) CHLORIDE FORMS IONS IN AQUEOUS SOLUTION

In Experiment 4, you were first asked to test distilled water.

- ☐ What can you say about the conductivity of distilled water?
- The bulb should remain unlit when the graphite rods are immersed in water. It seems, then, that water is a poor conductor of electricity.
- ☐ Were the solutions of sugar and copper(II) chloride good conductors of electricity?
- Only the solution of copper(II) chloride was a good conductor. It seems then that although water does not conduct electricity when it contains dissolved sugar, it does conduct when it contains dissolved copper(II) chloride.

What else did you observe when you tested the copper(II) chloride solution? You should have observed gas bubbles on the graphite rod wired to the *positive* terminal of the battery. This gas has a pungent smell which is often encountered in swimming pools and household bleach. It is chlorine. At the carbon rod wired to the *negative* terminal of the battery, there is little or no gas evolution, but a golden-brown metallic deposit forms on the part of the carbon rod that is covered by the solution.

- ☐ What do you think the metallic deposit is?
- It is metallic copper.

We see then, that the conduction of an electric current by a solution is accompanied by chemical changes at those parts of the circuit that make contact with the solution. In this sense, conduction by solutions is very different from conduction by metal wires. The process of chemical change or decomposition that a solution undergoes when it conducts electricity is called **electrolysis**.

Although the phenomenon was known in the eighteenth century, the first careful quantitative studies of it were made by Michael Faraday (Figure 23) in 1833, and he laid down much of the terminology still associated with it. He called the two parts of the circuit that make contact with the solution (in our case, the graphite rods) **electrodes**, and he also coined the word **electrolyte**, which may be defined as a substance that dissolves in a liquid and increases the ability of the liquid to conduct electricity. Thus CuCl_2 is an electrolyte in water, but sugar is a **non-electrolyte**.

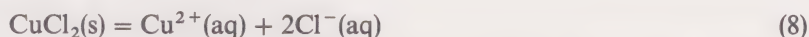
It also seemed clear to Faraday that if material was generated at the electrodes during conduction, the solution must contain particles that migrated to the two electrodes to produce the visible effects of electrolysis. These particles he called *ions*, and it was obvious that they were choosy about which electrode they moved towards. In the case of copper chloride, for example, one type of ion moved to the negative electrode before being deposited as metallic copper, whereas the other type moved to the positive electrode and was evolved as chlorine gas. Today we know of a key property of ions of which Faraday was unaware. It accounts for this preference for an electrode of a particular charge, and you should already be familiar with it from your study of mass spectrometry in Units 11–12.

- ☐ What is the property?
- Ions are electrically charged particles.

Thus a possible model of the copper(II) chloride solution begins to take shape: solid copper(II) chloride is electrically neutral, but when it is dissolved in water, it breaks up into separate copper and chlorine ions. During electrolysis, the copper ions move to the negative electrode where they are deposited as metallic copper; the chlorine ions move to the positive electrode where they are evolved as chlorine gas.

- What types of charge do the two kinds of ion have?
- Unlike charges attract one another. As copper ions move to the negative electrode, we assume that they are positively charged. Conversely, the ions of chlorine, conventionally called *chloride* ions, are negatively charged.

We can therefore describe what happens when copper(II) chloride dissolves in water by an equation:



The symbol (aq) after each charged particle or ion in Equation 8 indicates that the ions are in aqueous solution, as opposed to being, say, gaseous as they are in the mass spectrometer. Like all proper chemical equations, Equation 8 has been balanced with respect to chemical elements: there are two chlorines and one copper on each side of the equation. But this type of equation, which contains charged ions, must be balanced in an additional and important way: *it must be balanced with respect to charge*. This means that the sum of the electrical charges on each side of the equation must be the same. Thus the solid CuCl_2 on the left-hand side of the equation is neutral; it carries zero overall charge. Consequently, when the solid dissolves in water, the sum of the charges of the ions that are formed must also be zero. And you can see that it is. Each chloride ion on the right-hand side of the equation has been assigned a single negative charge. To balance the total of two negative charges of the two chloride ions, the single copper ion has been assigned a charge of +2: the total charge of the right-hand side of the equation, like that on the left, is then zero.

Next, having interpreted the dissolving of copper(II) chloride by Equation 8, we can settle on a satisfactory mechanism for the electrolytic process. Look at Figure 24. Conduction implies the movement of negative electrons from the negative to the positive pole of the battery, and as electrons flow easily in the wire leads and electrodes, but not in water, the crucial problem is the transfer of charge across the gap filled by the solution.

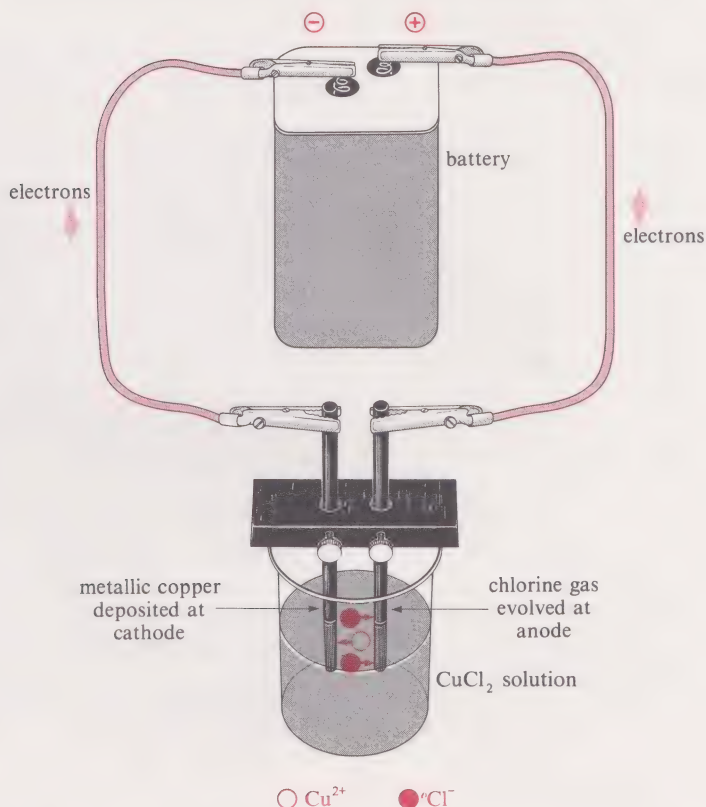


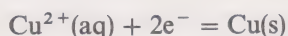
FIGURE 24 A mechanism, involving ions, that accounts for the conductivity of copper(II) chloride solution.

CATION

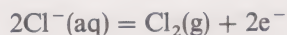
ANION

POLYATOMIC ION

If the Cu^{2+} ion migrates to the negative electrode, it can pick up two electrons and form an atom of copper metal, which is deposited on the surface of the carbon rod:



where we use the symbol e^{-} to represent a negatively charged electron. Simultaneously, two Cl^{-} ions, having migrated to the positive electrode, can surrender their electrons, which then move to the positive pole of the battery. The electrically neutral chlorine is now evolved at the positive electrode as the pairs of chlorine atoms which, as you know from Section 3.1.1, make up the molecules of chlorine gas:



The net result is that one atom of copper has been deposited at the negative electrode, one molecule of chlorine gas has been evolved at the positive electrode, and two electrons have been transferred by ions across the gap of the solution.

- ☐ Does the removal of ions at electrodes affect the initial electrical neutrality of the solution?
- No; one doubly charged Cu^{2+} ion and two singly charged Cl^{-} ions are removed simultaneously, so neutrality is maintained.

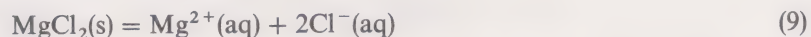
We end this Section with some new nomenclature. Besides introducing the term *ion*, Faraday called ions that moved towards the negative electrode, **cations** (pronounced 'cat-eye-ons') and those that moved towards the positive electrode, **anions** (pronounced 'an-eye-ons').

- ☐ What kinds of charge do cations and anions carry?
- Our explanation of electrolysis implies that cations are positive and anions negative. Consequently 'cation' is today just another word for positive ion, and chemists use the two terms interchangeably. Likewise, 'anion' is just another word for negative ion.

6.3 MORE SUBSTANCES THAT FORM IONS IN AQUEOUS SOLUTION

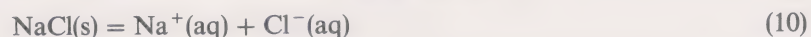
In Section 6, you were promised a classification of the twelve substances of Table 3 into two sets. So what other substances behaved like copper(II) chloride in Experiment 4? The compounds magnesium chloride (MgCl_2), sodium chloride (NaCl) and sodium sulphate (Na_2SO_4) all dissolve in water and when the solutions are incorporated in the circuit of Figure 22, the bulb lights up. Again, the phenomenon can be explained by the formation of aqueous ions through equations akin to Equation 8. How can such equations be written for MgCl_2 and NaCl ?

Like CuCl_2 , MgCl_2 contains two chlorines. In Equation 8, these formed two chloride ions, each carrying a single negative charge, so we will assume that this happens again:



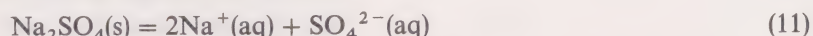
To balance the two negative charges carried by the two chloride ions, we give the single magnesium ion a double positive charge. The equation is now balanced with respect to charge because the sum of the charges is the same on both sides: in this particular case, it is zero.

Sodium chloride, NaCl , contains just one chlorine, so only one chloride ion is formed on the right-hand side of the equation:



The single sodium ion that is formed at the same time now needs just a single positive charge to create a balanced equation: the total charge is zero on each side.

Now let us turn to the more difficult case of sodium sulphate, Na_2SO_4 . How can one decide what ions this compound forms in aqueous solution? We start by giving you the answer:



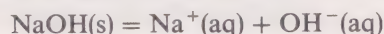
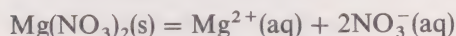
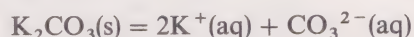
You will often need to write such equations for compounds of this type, and the way in which the formula of the solid compound is written down is usually a big help. First in the formula comes the part that forms positive ions. This usually consists of either hydrogen or metal atoms, and if so, then in all the examples in Units 13 to 16, this first part breaks down in water into monatomic positive ions (positive ions that contain just one atom).

How is this borne out by Equation 11?

The first part of the formula Na_2SO_4 consists of two sodium atoms, sodium being a metal. From our experience with NaCl , embodied in Equation 10, we know that sodium can form a singly charged cation in water. We therefore expect the two sodiums of Na_2SO_4 to turn up on the right-hand side of Equation 11 as $2\text{Na}^+(\text{aq})$. These ions are monatomic—they have been formed from just one sodium atom.

Having dealt with the first part, the sodium part of the formula Na_2SO_4 , we now turn to the remainder, the sulphate part, which consists of an SO_4 grouping. Equation 11 has been balanced by placing two negative charges against this grouping. This creates the second type of aqueous ion that is formed in the reaction, the sulphate ion, $\text{SO}_4^{2-}(\text{aq})$. As you can see, it is not monatomic, because it is made up from more than one atom.

Ions like sulphate ion, formed by charged groups of atoms bound together, are called **polyatomic ions**. Examples of other compounds, akin to sodium sulphate, which form polyatomic ions when they dissolve in water, include potassium carbonate, K_2CO_3 , magnesium nitrate, $\text{Mg}(\text{NO}_3)_2$, and sodium hydroxide, NaOH .



Note that the formula $\text{Mg}(\text{NO}_3)_2$ contains brackets that are new to you. The formula is spoken as 'm-g-n-oh-three-twice'. It implies that magnesium nitrate contains magnesium and nitrate (NO_3) in the ratio 1:2. The subscript '2' indicates two nitrate groups in the formula unit $\text{Mg}(\text{NO}_3)_2$.

Table 5 contains a list of some common cations and anions that exist in aqueous solution. Each ion is given its correct charge, and each polyatomic ion is named. Note that there is only one polyatomic cation in the Table, the ammonium ion.

TABLE 5 Some common aqueous ions

Monatomic cations	Monatomic anions	Polyatomic cation and anions
H^+	F^-	NH_4^+ (ammonium)
Li^+	Cl^-	OH^- (hydroxide)
Na^+	Br^-	NO_3^- (nitrate)
K^+	I^-	CO_3^{2-} (carbonate)
Mg^{2+}	S^{2-}	SO_4^{2-} (sulphate)
Ca^{2+}		PO_4^{3-} (phosphate)
Sr^{2+}		HCO_3^- (bicarbonate)*
Al^{3+}		

* As in solutions of domestic baking soda, NaHCO_3 , which is usually labelled sodium bicarbonate.

Before the end of this Section, we must turn to a problem thrown up by your experiments with the compounds NaCl , MgCl_2 and Na_2SO_4 . The electrolysis is not so easy to interpret as in the case of CuCl_2 . There, the copper part was produced at one electrode, and the chlorine part at the other.

By analogy, what might you expect in the cases of MgCl_2 and NaCl ?

Chlorine gas should appear at one electrode, and either magnesium metal or sodium metal at the other. In fact, this expectation is only partly fulfilled. You should indeed have seen and smelt the chlorine gas evolved at the positive electrode in both cases. However, instead of magnesium or sodium, a colourless gas with no smell (hydrogen) appears at the negative electrode.

In the case of sodium sulphate, the situation is even worse. Nothing that appears at the electrodes can be directly related to either the sodium or the sulphate ions in the solution. Around both electrodes, colourless gases with no smell appear. At the negative electrode, the product is hydrogen; at the positive electrode, oxygen. The source of these unexpected products is discussed on page 51. They show you that the prediction of the products formed during the electrolysis of aqueous solutions is rarely as straightforward as it is in the case of copper(II) chloride, and we shall not usually expect you to do it. What we *do* expect is that you should be able to write balanced equations for the dissolution of electrolytes in water when the products are ions such as those in Table 5. In addition, knowledge of the charges of the common ions listed in Table 5 allows you to write down the formulae of compounds such as calcium hydroxide or ammonium sulphate from their names alone.

SAQs 22 to 24 test your abilities in these fields, and you should try them when you have read the following summary.

SUMMARY OF SECTIONS 6 TO 6.3

1 Water is a poor conductor of electricity, but some substances, known as electrolytes, dissolve in water and greatly increase its conductivity.

2 The parts of the electrical circuit that make contact with a conducting solution are called electrodes. During conduction, chemical changes occur at the electrodes, the total chemical process being known as electrolysis.

3 The electric current is carried through the solution by charged particles called ions, which are made up from one or more atoms. These ions are formed by the breakdown of the electrolyte when it dissolves in the water. This breakdown can be described by a chemical equation, which is balanced with respect to both chemical elements and charge.

SAQ 22 The following substances are electrolytes: lithium iodide, LiI(s) ; calcium sulphate, $\text{CaSO}_4\text{(s)}$; sodium phosphate, $\text{Na}_3\text{PO}_4\text{(s)}$; hydrogen iodide, HI(g) ; iron(III) chloride, $\text{FeCl}_3\text{(s)}$; aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3\text{(s)}$. Write balanced equations to describe what happens when each one of these substances dissolves in water.

SAQ 23 Use Table 5 to write down the chemical formulae of the following solid compounds: aluminium chloride, magnesium sulphate, ammonium sulphate, calcium hydroxide, calcium phosphate.

SAQ 24 The gas hydrogen chloride, HCl , dissolves in water. If the solution is then placed in the beaker in Figure 22, the bulb lights up, and gases are evolved at each electrode.

(a) Write an equation for the dissolution of HCl .

(b) Assuming that the electrolysis follows the simple pattern observed with copper(II) chloride, write equations for the reactions that take place at the electrodes.

6.4 THE CONCEPT OF AN IONIC SUBSTANCE

You have now completed your experiments with the compounds CuCl_2 , MgCl_2 , NaCl and Na_2SO_4 . Table 6 records information about these substances, and about two other solids, sodium bromide and potassium iodide. Together, these compounds make up six of the twelve substances that we have chosen to study.

Use your experimental results to complete Table 6 by filling in the blank spaces.

TABLE 6 The properties of six of the twelve chosen substances

Substance	Dissolves easily in water?	Aqueous solution conducts well?	Dissolves easily in heptane?	Melting temperature	Liquid conducts well?
CuCl_2			no	high	yes
MgCl_2			no	high	yes
Na_2SO_4			no	high	yes
NaCl			no	high	yes
NaBr	yes	yes	no	high	yes
KI	yes	yes	no	high	yes

Now that you have done this, you should see evidence that the six compounds have much in common.

What is this evidence?

In each column, the answers to the questions are the same for all six compounds. Let us look at each column in more detail.

Columns 2 and 3 tell you that the solids are electrolytes in water, a fact that we have explained by the formation of aqueous ions. The next column records the fact that the six substances have a negligible solubility in heptane. Column 5 tells us that all of the compounds have high melting temperatures; by 'high', we mean greater than about 250°C . By contrast, substances like water and heptane, which are liquids at room temperature, have 'low' melting temperatures (well below 200°C).

The final column is very important, although unfortunately it records the results of experiments that need higher temperatures than you can safely reach at home. It tells us that after the six substances have melted, the liquids (or melts) that are produced conduct electricity.

How can this be explained?

Just as we have explained the conductivity of aqueous solutions by the formation of aqueous ions, we explain the conductivity of the liquids by the existence of ions in the melts. Thus we argue that molten sodium chloride contains the ions Na^+ and Cl^- in a 1 : 1 ratio. Likewise, molten magnesium chloride contains the ions Mg^{2+} and Cl^- in a 1 : 2 ratio.

Would you expect the products produced at each electrode during conduction to be the same as when the aqueous solutions are electrolysed?

As noted in Section 6.3, the electrolysis of the aqueous solutions unexpectedly produces hydrogen gas rather than sodium or magnesium at the negative electrode. Since NaCl and MgCl_2 contain no hydrogen, the hydrogen gas must originally have come from the water in the aqueous solutions. The involvement of water molecules in the electrode reactions also accounts for the unexpected production of oxygen at the positive electrode during the electrolysis of sodium sulphate solutions. But in molten NaCl and

IONIC SUBSTANCE

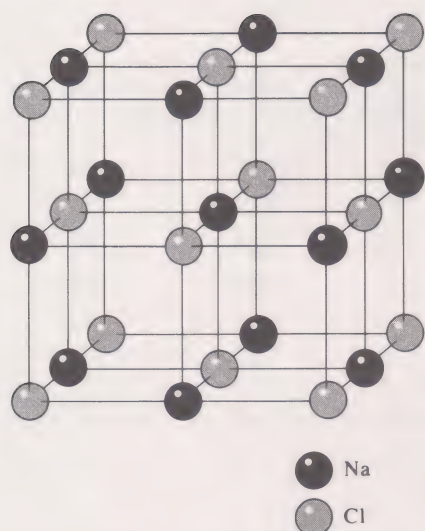
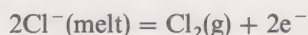


FIGURE 25 The structure of sodium chloride. The lines shown joining sodiums and chlorines are inserted merely to show the relative positions of the ions. They are not meant to represent electron-pair bonds of the type described in Section 7.4. The distance between ions in the crystal is 281 pm (1 picometre (pm) = 10^{-12} m = 10^{-3} nm).

MgCl_2 there is no water present. Thus we expect sodium and magnesium metals to be formed at the negative electrode, with chlorine gas formed at the positive electrode, e.g.



This time our expectation is fulfilled, and in fact, it is by the electrolysis of molten NaCl and MgCl_2 that sodium and magnesium metals are made in industry. Currently about a third of a million tons of magnesium is made in this way each year. It is used to make, among other things, helicopters, space satellites, space stations and racing cars.

We see therefore that both in the molten state and in aqueous solution, we can think of the six compounds as a collection of ions. But why stop there? Could this also be true in the solid state? With this in mind, let us look at the structure of solid sodium chloride. The structure is built up from cubic arrangements of the kind shown in Figure 25. The dark spheres represent sodiums and the light spheres chlorines. A real crystal of salt is built up by joining millions of such cubes through faces into a block. Two cubes so joined are shown in Figure 26. Any cube deep within a real crystal is joined thus through its six faces to six others, which then completely surround it. In such a structure, the immediate environment of any sodium can be seen by looking at the example at the centre of Figure 25. It is surrounded by six chlorines at the centres of the six cube faces.

In a crystal of sodium chloride, what is the immediate environment of any chlorine?

Look at the chlorine at the centre of the joined face in Figure 26. It is surrounded by six sodiums in just the way that any sodium is surrounded by six chlorines. Suppose now that we think of what we have called sodiums and chlorines as Na^+ and Cl^- ions. The structure then seems very reasonable because each ion surrounds itself by ions of opposite charge. Strong attractive forces between the positive and negative ions hold the structure together, so a lot of heat energy is needed to break it apart. This accounts for the high melting temperatures of such solids (for NaCl the value is 801°C), and also for the unwillingness of the structure to break apart and dissolve in solvents such as heptane, petrol or dry-cleaning fluid.

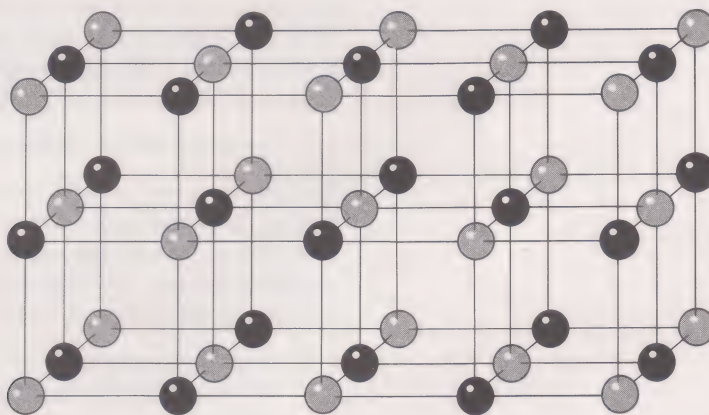


FIGURE 26 Two of the units in Figure 25 joined through a cube face.

Note that in Figure 25, the six chlorines around any sodium are all the same distance away from the sodium. This means that there are no grounds for singling out one of them, and coupling it with the sodium to create an NaCl molecule: the structure provides no evidence for the existence of discrete NaCl molecules. In this case, the formula NaCl merely implies that the compound contains equal numbers of sodiums and chlorines or, according to the model that we have proposed, of Na^+ and Cl^- ions.

Two more of the six substances in Table 6, NaBr and KI , have structures just like that of NaCl in Figure 25. Thus out of this Section comes a picture of a class of compounds that we shall call **ionic substances**. The ideal ionic substance:

(i) is a solid with high melting and boiling temperatures, and the melt readily conducts electricity.

- (ii) will, if it dissolves significantly in water, form an aqueous solution that readily conducts electricity.
- (iii) has a structure in which the assumed ions tend to surround themselves with ions of opposite charge, and in which discrete molecules with the same empirical formula as the solid cannot legitimately be singled out.
- (iv) has a very low solubility in organic solvents such as heptane, petrol and dry-cleaning fluid, which are composed mainly or wholly of hydrogen and carbon atoms.

Many chemical compounds meet this idealized description fairly closely, and this makes the classification a very useful one. They include the six compounds in Table 5.

Finally, note that property (ii) is conditional upon the substance being readily soluble in water. It is important to specify this condition because many substances that can usefully be classified as ionic (because they meet criteria (i), (iii) and (iv)) have a very low solubility in water. They include, for example, calcium carbonate, CaCO_3 , which occurs naturally as chalk, and calcium fluoride, CaF_2 . The constituent ions are Ca^{2+} and CO_3^{2-} in the first case, and Ca^{2+} and F^- in the second (compare Table 5). When these substances are added to water, whatever dissolves forms aqueous ions, but the amount that dissolves is so small that the conductivity of the water is little changed.

Nevertheless, many ionic solids do dissolve easily in water, as Table 6 implies. This raises an important question. We have argued that because the ions in the solids are held together by strong attractive forces, they do not readily separate and dissolve in an organic solvent such as heptane. But if this is the case, why do so many ionic solids dissolve in water? This question is taken up in Section 7.6. But first, we discuss those substances in Table 3 that are *not* ionic.

6.5 THE SIX REMAINING SUBSTANCES

Six of our twelve substances have been classified as ionic compounds. Now let us turn to the remaining six. None of their properties can be understood by arguing that they consist of ions. Water and heptane are liquids at room temperature, and your electrolysis experiments have shown you that chlorine is a gas. These three substances must therefore have low melting temperatures. Chlorine can be liquefied by cooling it below -35°C , but, like water and heptane, the liquid does not conduct electricity. Sugar is a solid, but as you may sometimes have observed if you have dropped it on a hot plate, it melts at a relatively low temperature (185°C). Again, the liquid, like the aqueous solution, is a very poor conductor of electricity. These observations are summarized in Table 7.

TABLE 7 The properties of the remaining six of the twelve chosen substances

Substance	Dissolves easily in heptane?	Melting temperature	Liquid conducts well?
sugar		low	no
water		low	no
heptane		low	no
chlorine		low	no
bromine			
iodine			

Before considering any classification of the six substances, you must gather the information that will enable you to complete Table 7. As this table contains no entries at all for bromine and iodine, this will be done mainly

MOLECULAR COVALENT
SUBSTANCE

through experiments on these two substances. In Experiment 4, you made chlorine by the electrolysis of an aqueous solution of an alkali metal chloride (NaCl). You will now make bromine and iodine by the electrolysis of aqueous solutions of an alkali metal bromide and iodide.

EXPERIMENT 5 PREPARATION OF BROMINE AND IODINE

TIME

about 40 minutes

KIT ITEMS

You need the apparatus shown in Figure 21, which you used in Experiment 4, and

Chemical tray
heptane

potassium iodide

sodium bromide

dilute sulphuric acid (1 mol l^{-1})

1,1,1-trichloroethane

Tray A

dropping pipette

glass stirring rod

rubber stoppers (four)

rubber teat for dropping pipette

test-tubes (four)

Tray B

beakers, 100 cm^3 (two)

Tray C

measuring spoon (spatula-type)

test-tube rack

PART 1

Fill the beaker about one-quarter full of distilled water. Attach the teat to the dropping pipette, draw up a little sulphuric acid, and add about five drops to the water in the beaker. Now add two 'spoons' of sodium bromide, and stir with the glass rod until the solid has dissolved. Incorporate the beaker and solution in the circuit of Figure 22, just as you did in Experiment 4. The bulb should light up. Allow current to pass for 4 minutes, and after 2 minutes, *cautiously* smell the air in the beaker. Describe in your Notebook any changes in the solution, and also what happens at the electrodes.

When the 4 minutes are up, remove the electrodes, rinse them with water, and set them aside. Then fill two test-tubes about one-quarter full of the solution. To one, add about a 1 cm depth of heptane; to the other about a 1 cm depth of 1,1,1-trichloroethane.

Now stopper both test-tubes and invert them several times, holding the stoppers in with your thumb. Allow the two layers in each tube to settle, and note their colours [heptane (the upper layer) and 1,1,1-trichloroethane (the lower layer) do not mix with water].

PART 2

Repeat Part 1, using potassium iodide in place of sodium bromide, and the second beaker.

During electrolysis, the production of bromine and iodine is marked by dark colourations at the surface of the positive electrode. These products then dissolve in the bulk of the solution. Both bromine and iodine are readily soluble in heptane or 1,1,1-trichloroethane, a fact proved by the capacity of these solvents to extract some dissolved bromine and iodine from the aqueous layer to give yellow and violet solutions, respectively.

In both experiments, the smell of the halogen should have been detectable. This suggests that the elements are rather easily vaporized.

☐ Have you seen any other evidence that this is true for iodine?

☒ The iodine in your Experiment Kit may have leaked out of its bottle.

In fact, iodine melts at only 114°C , and boils at 185°C . Bromine is even more easily vaporized than iodine. When pure, it is a dark red liquid, which boils at only 59°C . *Neither liquid bromine nor liquid iodine readily conducts electricity.*

Now fill in the blank spaces against bromine and iodine in Table 7.

Finally, we note that, like bromine and iodine, chlorine is soluble in heptane, and that heptane, like any other liquid, is readily soluble in itself. It is also soluble in petrol, dry-cleaning fluid and 1,1,1-trichloroethane. You can test the solubility in 1,1,1-trichloroethane if you wish. By contrast, both

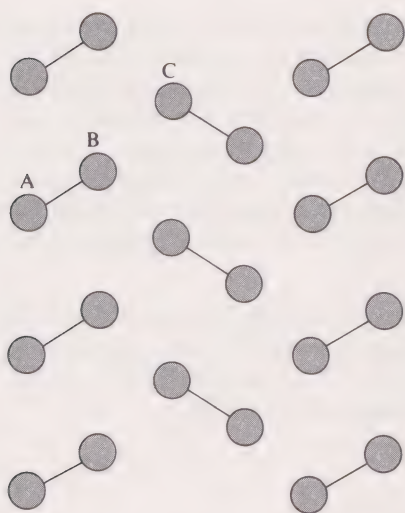


FIGURE 27 A layer of the structure of solid iodine. The iodine atoms can be grouped into pairs on the basis of internuclear distance. Thus, the distance BA is only 268 pm, but BC is 356 pm. The pairs of iodine atoms are referred to as diatomic molecules.

water and sugar have very low solubilities in these solvents. In the case of water, you saw evidence of this in Experiment 5, when aqueous solutions would not mix with heptane or 1,1,1-trichloroethane.

Now complete Table 7.

When you completed Table 6 in Section 6.4, the answers to the question in all columns were identical.

Is this true of Table 7?

Nearly, but not quite: neither sugar nor water is readily soluble in heptane. Nevertheless, the similarities in the properties of the six substances are considerable. Let us therefore look for other evidence that they can be classified together.

6.6 THE CONCEPT OF A MOLECULAR COVALENT SUBSTANCE

In Section 6.4, the structure of one of our six ionic compounds proved very illuminating. Perhaps, therefore, the structure of one of the six substances in Table 7 will help in explaining the common properties of this second group. We choose solid iodine, and its structure is shown in Figure 27. It contains pairs of atoms separated by what is, on a molecular scale, the relatively short distance of 268 pm. Short distances between atoms usually imply that there is a strong bond between them. However, the shortest distance that one can pick out *between the different pairs* is relatively large (356 pm). Thus solid iodine consists of tightly bound pairs of atoms (diatomic molecules), with weaker forces acting between the pairs.

- ☐ Can you explain the low melting and boiling temperatures of iodine?
- ☒ Because the pairs are held together in the solid state by weak forces, relatively little heat energy is needed to separate them and create an iodine liquid or vapour containing diatomic molecules. This ease of separation also allows the crystal to fall apart and dissolve in solvents such as heptane and petrol.
- ☐ Why is it that neither molten iodine, nor a solution of iodine in heptane, conducts electricity?
- ☒ When the crystals fall apart, they form I_2 molecules. No ions are present in either the melt or the solution.

All this is very different from the case of sodium chloride in Section 6.4. Discrete NaCl molecules could not be picked out in the structure of the solid, and we argued that ions were present in the solid state, melt and aqueous solution.

Thus to set alongside the class of ionic substances, we have a new class which we shall call **molecular covalent substances**. The ideal molecular covalent substance:

- (i) has relatively low melting and boiling temperatures; at room temperature, some molecular covalent substances are solids, some are liquids and some are gases.
- (ii) does not conduct electricity in the liquid state.
- (iii) has a structure in which discrete molecules, with the same empirical formula as the substance, are separated from each other by what are relatively large distances on a molecular scale.
- (iv) dissolves readily in solvents such as heptane, petrol and dry-cleaning fluid to give solutions that do not conduct electricity. Note, however, that this characteristic is the least crucial of the four. Thus water and sugar fall short of the ideal pattern because they lack this property, but they are still classified as molecular covalent substances because they possess the other three.

Other molecular covalent liquids are chloroform (CHCl_3) and nitrogen trichloride (NCl_3). Gases in this class include nitrogen (N_2) and oxygen (O_2), ammonia (NH_3), natural gas or methane (CH_4), carbon dioxide (CO_2), hydrogen chloride (HCl), and another halogen, fluorine (F_2).

The twelve substances that we chose to study have now been divided into two classes. Half are ionic substances, and the remainder are molecular covalent. In the first category come CuCl_2 , MgCl_2 , NaCl , Na_2SO_4 , NaBr and KI ; in the second H_2O , Cl_2 , Br_2 , I_2 , heptane and sugar. Look now at the chemical elements of which each class is composed, and then study their positions in Figure 28.

For each class, describe how the constituent elements are distributed in the Periodic Table.

I	II											III	IV	V	VI	VII	0
																H	
													C		O		
Na	Mg														S	Cl	
K										Cu					Br		
															I		

The six molecular covalent substances are composed solely of non-metallic elements that lie close together at the right-hand end of the Periodic Table. The six ionic substances all contain both metallic and non-metallic elements, the latter lying well to the right, and the metallic elements being well separated from them to the left. Indeed, with the exception of CuCl_2 , our six ionic substances are a combination of chemical elements from the *extreme* left of the Periodic Table with those from the *extreme* right.

How are these two kinds of chemical element partitioned between the ions of which the ionic substances are composed?

The positive ions are monatomic and composed of metallic elements (Cu^{2+} , Mg^{2+} , Na^+ , K^+); the negative ions contain non-metallic elements, being either monatomic (Cl^- , Br^- , I^-) or polyatomic (SO_4^{2-}).

We have elicited these generalizations from the properties of only a few substances, and we emphasize that they are only tendencies—they are by no means always valid. Nevertheless they contain much truth, and you will find them listed in the summary that follows this Section. They illustrate the way in which patterns become apparent when a discussion of the properties of chemical substances is organized with reference to the Periodic Table. As you will see next in Section 7, these patterns point us towards explanations of the chemical formulae of compounds and of the forces that hold the compounds together.

SUMMARY OF SECTIONS 6.4 TO 6.7

1 Many important chemical substances can be classified as either ionic or molecular covalent.

2 An ideal ionic substance is a solid at room temperature, has high melting and boiling temperatures, conducts electricity when molten and has a very low solubility in solvents such as heptane, petrol and dry-cleaning fluid. Its structure is one in which the assumed ions of opposite charge are juxtaposed, and in which discrete molecules with the empirical formula of the substance cannot be singled out.

3 An ideal molecular covalent substance has low melting and boiling temperatures, and a structure in which discrete molecules with the empirical formula of the substance can be singled out. It often dissolves readily in solvents such as heptane, petrol and dry-cleaning fluid, and these solutions, like the molten substance, do not conduct electricity.

4 When metals on the left of the Periodic Table combine with non-metals on the right, ionic substances tend to be formed. When this happens, the metallic element often takes on the form of a monatomic cation and the non-metallic elements end up as a monatomic or polyatomic anion.

5 When non-metallic elements on the right of the Periodic Table combine with each other, molecular covalent substances are often produced.

SAQ 25 Which of the following substances would you classify as ionic, and which molecular covalent? Give your reasons.

Substance	Dissolves easily in water?	Dissolves easily in heptane?	Aqueous solution conducts well?	Melting temperature	Liquid conducts well?
TNT	no	yes	—	low	no
strontium chloride	yes	no	yes	high	yes
lithium phosphate	no	no	—	high	yes
ethanol (alcohol)	yes	yes	no	low	no

SAQ 26 Five of the following ten substances are commonly described as ionic, and five as molecular covalent: LiH , HF , SF_2 , SrF_2 , LaBr_3 , PBr_3 , TiO_2 , SO_2 , P_2O_3 , Al_2O_3 . By using only the formulae, and Figure 17, assign each compound to the appropriate category.

7 ELEMENTARY THEORIES OF CHEMICAL BONDING

Ionic and covalent substances are important because they are an essential preliminary to a simple theory of chemical bonding. When two elements react to form a compound, their atoms tend to combine in a particular ratio. For example, sodium and chlorine react to yield NaCl , not NaCl_2 or NaCl_3 . Likewise, the product of the reaction of hydrogen and oxygen is H_2O , not HO or HO_2 . But *why* is there such a strong preference for the combinations NaCl and H_2O ? Theories of chemical bonding supply answers to questions like this.

ELECTRONIC CONFIGURATION
OF A NOBLE GAS

IONIC BONDING

To form a compound, the different atoms have to make contact with one another and bond together. An atom consists of a nucleus surrounded by electrons, so initial contact between atoms occurs in the vicinity of the outer electrons. Not surprisingly, therefore, the outer electronic configuration strongly influences the way one kind of atom bonds to another. We begin by looking at a very important type of outer electronic configuration.

7.1 THE NOBLE GASES

The simplest theories of chemical bonding are based on the observation that the elements of Group 0, the noble gases, are extraordinarily unreactive. These elements are helium, neon, argon, krypton, xenon and radon, and you met them in the TV programme 'Elements discovered'. They are all monatomic gases: that is, they exist as He atoms or Ne atoms, not as He₂ or Ne₂ molecules. They do not react with the common laboratory chemicals. Indeed, they are all unaffected by molten sodium, which is usually extremely reactive, and helium, neon and argon do not even react with hot fluorine, a substance that attacks nearly every other element. Since 1962 some compounds of xenon, krypton and radon have been prepared, for example XeF₄, XeO₃, and KrF₂, but the overall impression of a chemically very unreactive group is correct.

We describe this chemical inertness of the Group 0 elements by saying that the noble gases are *stable* with respect to chemical reactions. Now when atoms react, their outer electronic configurations are disturbed. It follows that the electronic configurations of the noble gases must be particularly stable to disturbance.

What evidence have you seen of this in Units 11–12?

Figure 29 (from Units 11–12) shows that the ionization energies of the noble gases are unusually large, that is, removal of an electron from a noble gas atom is especially difficult. This suggests that the **electronic configuration of a noble gas** is unusually stable with respect to the loss of an electron.

Simple theories of chemical bonding assume that the electronic configurations of the noble gases are especially stable, and that many elements tend to attain noble gas electronic configurations in their chemical reactions.

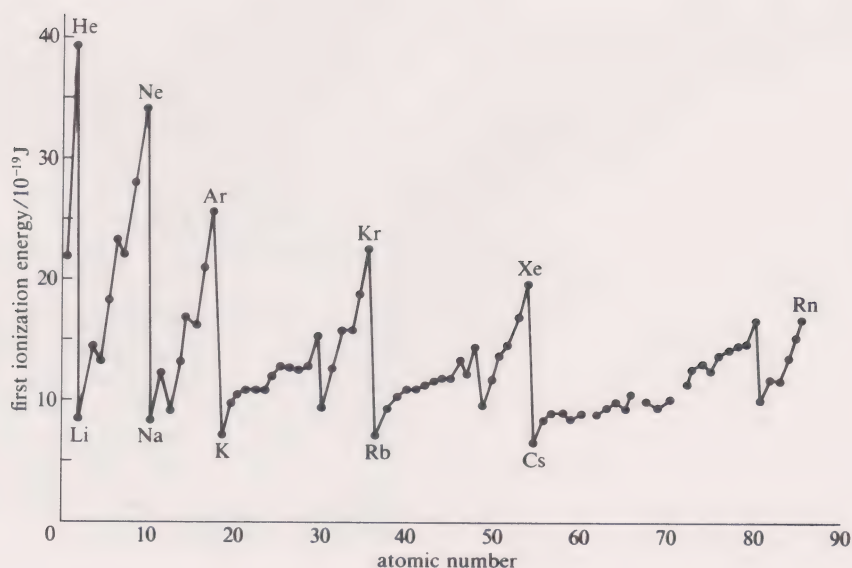


FIGURE 29 Ionization energies of the atoms of the chemical elements.

According to this assumption, the noble gases are chemically inert because they already have noble gas electronic structures. But how can one element attain the electronic structure of another? According to the elementary theories of bonding there are two ways. The first way is appropriate when dealing with the ionic substances of Section 6.4; it is called *electron transfer*. The second way is appropriate when dealing with covalent compounds, some of which you met in Section 6.6; it involves *electron sharing*.

7.2 IONIC BONDING

In Section 6.4, we explained the properties of ionic substances by arguing that they contain ions. But why do the ions have the charges that they do? Why, for example, does the sodium in sodium chloride have just one positive charge, rather than, say, two negative charges?

In Section 7.1 you saw that the noble gases have stable electronic configurations. Now the alkali metals, the Group I elements, all have the electronic structure of a noble gas *plus* one extra electron. If this extra electron is removed in a chemical reaction, a positively charged ion (cation) will be formed and this ion will have the electronic configuration of a noble gas atom. Thus, for example, lithium has the electronic configuration $1s^2 2s^1$; by loss of its 2s electron, it forms the lithium ion Li^+ and attains the noble gas structure of helium ($1s^2$):

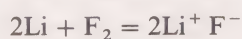


- ☐ What is the electronic configuration of the sodium ion Na^+ ? To what noble gas does this configuration correspond?
- The configuration of Na^+ is that of neon: $1s^2 2s^2 2p^6$.
- ☐ What is the important difference between a lithium ion and a helium atom?
- A lithium ion is positively charged, whereas a helium atom is neutral: lithium has three protons in its nucleus, whereas helium has only two. The superscript on the symbol for the lithium ion records the single excess positive charge.

Consider now the Group VII elements, the halogens. They all have the electronic configuration of a noble gas *less* one electron. By addition of one electron, for example in a chemical reaction, a negatively charged ion (anion) will be formed, which will have the electronic configuration of a noble gas atom. Thus, for example, fluorine ($1s^2 2s^2 2p^5$) will form a fluoride ion F^- , with the electronic structure ($1s^2 2s^2 2p^6$) of neon.

- ☐ What is the electronic configuration of the chloride ion, Cl^- ? To what noble gas does this configuration correspond? What does the superscript minus stand for?
- $1s^2 2s^2 2p^6 3s^2 3p^6$, the configuration of argon. The chlorine now has 18 electrons (with negative charges), but there are still only 17 positively charged protons in the nucleus. Consequently, the chlorine now has one excess negative charge, as the minus sign of Cl^- shows.

Thus you can envisage that when the metal lithium and the gas fluorine react to form lithium fluoride, which is a colourless compound resembling common salt, an electron is transferred from each lithium atom to each fluorine atom, with the formation of the corresponding ions:



The electrostatic attraction between the positive lithium ions and negative fluoride ions in lithium fluoride gives rise to **ionic bonding**.

We now know that lithium ions have a single positive charge, and fluoride ions a single negative charge because these charges give each ion a noble

SINGLE BOND

DOUBLE BOND

TRIPLE BOND

COVALENT BONDING

LEWIS STRUCTURE

gas configuration. At the same time, this explains why lithium fluoride has the formula LiF : the compound must be neutral and this can only be achieved by combining equal numbers of the oppositely charged ions.

☐ Write down the electronic configuration of magnesium. How could magnesium most easily attain the electronic configuration of a noble gas? What therefore is the symbol for the magnesium ion? What would be the formula for magnesium fluoride?

■ $1s^2 2s^2 2p^6 3s^2$. Loss of the two $3s^2$ electrons would give a Mg^{2+} ion with the electronic configuration of neon, and two excess positive charges. So to be neutral, magnesium fluoride must be MgF_2 , that is, $\text{Mg}^{2+}(\text{F}^-)_2$. This second formula records the fact that for every magnesium ion in the compound, there are two fluoride ions.

In summary, the alkali metals (Group I) form compounds containing singly charged positive ions. Magnesium in Group II forms compounds containing the ion Mg^{2+} . The halogens (Group VII) form compounds containing singly charged negative ions, generally called halide ions. All these ions have noble gas electronic configurations. Their charges are such that the alkali metals must form halides of the type M^+X^- , and Group II metals like magnesium, halides of the type $\text{M}^{2+}(\text{X}^-)_2$.

What is the charge of the oxygen in magnesium oxide?

Oxygen has the electronic structure $1s^2 2s^2 2p^4$. It can attain the noble gas structure (neon) by acquiring two electrons, that is, by forming an O^{2-} ion. Oxygen in magnesium oxide thus has a charge of -2 and the formula of the oxide is MgO , corresponding to $\text{Mg}^{2+}\text{O}^{2-}$. The charges balance each other, and as before, the compound is electrically neutral.

7.3 MOLECULAR COVALENT SUBSTANCES AND VALENCY

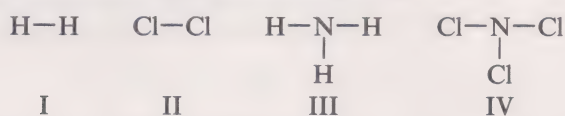
As you saw in Section 6.6, molecular covalent substances have properties that cannot be understood by assuming the existence of ions. Instead, they contain discrete molecules. As examples of this type of substance, we cited, among others, chlorine (Cl_2), oxygen (O_2), nitrogen (N_2), hydrogen (H_2), water (H_2O), carbon tetrachloride (CCl_4), nitrogen trichloride (NCl_3), ammonia (NH_3), methane (CH_4) and carbon dioxide (CO_2). All contain discrete molecules with the formula indicated.

In Section 3.3, you were shown how the formulae of these substances could be understood by assigning a fixed *valency* to the atoms of nitrogen, oxygen, hydrogen, chlorine and carbon.

☐ What valencies were assigned to each of these atoms?

■ One to hydrogen and chlorine, two to oxygen, three to nitrogen and four to carbon.

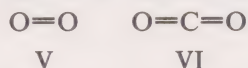
In Section 3.3, the valency was just a number that could be used to predict the formulae of compounds. However, when dealing with molecular covalent substances, it can be used to build up a schematic diagram of the molecule. Consider, for instance, the molecules H_2 , Cl_2 , NH_3 and NCl_3 . They can be represented by the following diagrams:



In these diagrams of the molecules, the atoms are linked together by lines known as *bonds*. The number of bonds issuing from each atom is equal to its valency. Thus three bonds spring out of each nitrogen atom, and one from each hydrogen or chlorine atom.

ITQ 6 Represent molecules of the compounds hydrogen chloride (HCl), methane (CH₄), carbon tetrachloride (CCl₄) and water (H₂O) in this way.

The atoms in the molecular diagrams or *structures* that you have seen so far have been linked by single valency lines or **single bonds**. This however is by no means always the case. Consider the oxygen molecule (O₂) and carbon dioxide (CO₂). To ensure that oxygen and carbon have their familiar valencies of two and four respectively, the molecules are drawn as follows:



In these examples, atoms are linked by two valency lines: they are said to be held together by **double bonds**.

- ☐ Draw a diagram of the N₂ molecule in which nitrogen has its common valency of three.
- N≡N; here the two atoms are linked by a **triple bond**.

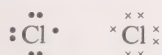
To summarize, you have been shown how to draw diagrams of the molecules in molecular covalent compounds in which each atom forms a number of bonds equal to its assigned valency. But what is the nature of the bonds which hold the atoms together, and why do the carbon, chlorine, hydrogen, nitrogen and oxygen atoms have the valencies that they do?

7.4 COVALENT BONDING

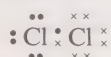
The properties of chlorine, Cl₂, are nothing like those of an ionic substance such as NaCl. However, even if we ignore this and try to give the Cl₂ molecule an ionic form, we cannot give all the constituent ions a noble gas configuration. Suppose we say that one of the chlorines in the Cl₂ molecule is a Cl⁻ ion with the electronic configuration of argon.

- ☐ What charge and electronic configuration will the other chlorine have?
- To maintain neutrality, it must be Cl⁺. This ion has the configuration of the sulphur atom.

In 1916, a solution to this sort of problem was proposed by an American chemist, Gilbert Lewis (Figure 30). He suggested that bonds could be formed between atoms by *sharing* pairs of electrons and that each shared pair constituted a **covalent bond**. He pointed out that this provided a means by which atoms in many compounds could attain noble gas structures. Thus, we can represent two chlorine atoms by the symbols



where the dots on one atom and the crosses on the other represent the seven outer electrons (3s²3p⁵). We then write the chlorine molecule Cl₂ as:



This type of diagram is called a **Lewis structure**. By convention, the outer electrons around the atoms are grouped in pairs. The pair of electrons that falls between the two chlorines is counted towards the electronic configurations of *both*. The pair of electrons thus shared between the atoms constitutes a chemical bond.

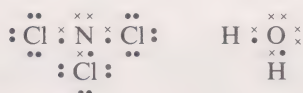
- ☐ What electronic configuration is thereby achieved by the two chlorines in the Cl₂ molecule?
- Each chlorine gains one electron. Both atoms thus attain the electronic configuration of argon, that is, they both have eight outer electrons (3s²3p⁶).



FIGURE 30 Gilbert Lewis (1875–1946). An American who in 1926 coined the word ‘photon’ for a quantum of electromagnetic radiation. The most famous chemist to be passed over for a Nobel Prize, he is best known for his idea of the electron-pair bond. He liked cigars, was promoted to Lieutenant-Colonel for training of gas officers in the Great War, and died of heart failure while doing an experiment.

Because one pair of electrons is involved in the Lewis structure, the bond is a *single bond*. The electron pair is therefore an electronic interpretation of the single bond line drawn between the two chlorine atoms in structure II.

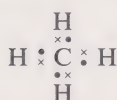
As further examples, consider the molecules NCl_3 and H_2O . Nitrogen has five outer electrons ($2s^2 2p^3$), hydrogen has one ($1s^1$), and oxygen has six ($2s^2 2p^4$). Suppose we represent the outer electrons on the nitrogen and oxygen atoms by crosses, and those on the hydrogen and chlorine atoms by dots. Then each atom attains a noble gas configuration in the Lewis structures:



What noble gas configurations are attained by nitrogen, oxygen and hydrogen in these structures?

In NCl_3 , the nitrogen gains one electron from each of the three electron pairs that it shares with chlorine. Its eight outer electrons then correspond to the electronic configuration of neon ($2s^2 2p^6$). Note that the three shared electron pairs needed to give nitrogen this configuration explain why the valency of nitrogen is three in structure IV on p. 60. The neon configuration is also attained by oxygen in the water molecule. Each hydrogen gains one electron from the single electron-pair bond that it forms with oxygen and attains the electronic configuration of helium ($1s^2$).

- Now write out a Lewis structure for the methane molecule, CH_4 .
- Carbon has four outer electrons ($2s^2 2p^2$). It can attain the electronic configuration of neon ($2s^2 2p^6$) by gaining another four electrons from four shared electron pairs:



In this structure, each hydrogen again attains the helium electronic configuration.

So far, any two atoms in our Lewis structures have been held together by just one electron-pair bond. Sometimes however, two or three pairs may be involved.

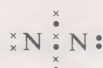
Draw the Lewis structure corresponding to structure VI for CO_2 on p. 61.

Each atom can attain the noble gas configuration of eight outer electrons if each oxygen is tied to the central carbon by not one but *two* electron-pair bonds.



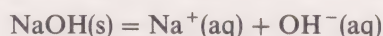
The two electron pairs between each oxygen and the central carbon are an electronic interpretation of each carbon-oxygen *double* bond in structure VI. As the examples of CO_2 and CH_4 show, carbon has a valency of four because, when it exercises that valency, it attains the neon electronic configuration.

As noted in Section 7.3, an example of a *triple* bond is supplied by the nitrogen gas molecule, $\text{N}\equiv\text{N}$. The Lewis structure is:



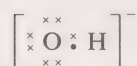
The existence of covalent bonds is not confined to neutral molecules. Such bonds also hold together the polyatomic ions that you met in Section 6.3.

For example, sodium hydroxide dissolves in water and forms aqueous ions:



Sodium hydroxide is an ionic compound, Na^+OH^- , but the hydroxide ion it contains is held together by a covalent bond. We can put an OH^- ion together by bonding an O^- ion to a hydrogen atom.

- ☐ How many outer electrons will an O^- ion have?
- Seven. An oxygen *atom* has six ($2s^2 2p^4$) electrons and one more is added for the negative charge.
- ☐ Now draw a Lewis structure for OH^- .
- A single bond now gives both oxygen and hydrogen a noble gas configuration:



The negative charge is now part of the whole oxygen–hydrogen complex, so we put it outside brackets drawn around the Lewis structure.

At this point, you could be forgiven for thinking that the bonding and formulae of *all* chemical compounds can be explained by assuming that the atoms tend to attain noble gas configurations. *But this is very far from being true.* For instance, the theory cannot account for the existence of transition element compounds such as FeCl_2 and CuO , or for sulphur trioxide, SO_3 . Nevertheless, it can, as you have seen, be usefully applied to many substances, and we now emphasize this by extending it to a new type of material.

7.5 EXTENDED COVALENT SUBSTANCES

Your study of covalent substances has so far been confined to compounds or elements that are composed of discrete molecules. But not all covalent substances are like this. This point can be demonstrated by diamond, one of the two forms of the element carbon. Although a different kind of covalent substance, its structure can be understood using the principles of Section 7.4. Diamonds are held together by C—C covalent bonds.

- ☐ How many bonds of this type will each carbon atom form?
- Four. We showed in Sections 3.3 and 7.3 that carbon has a valency of four, and in Section 7.4 how in forming four single covalent bonds, carbon attained the electronic structure of neon.

In diamond, each atom forms four C—C electron-pair bonds, which point towards the corners of a regular tetrahedron (a pyramid with triangular base and sides). A fragment of the diamond structure is shown in Figure 31. The C—C bonds are very strong, and you will notice that they spread out symmetrically through the structure in all directions. It is therefore very difficult to break into the structure with, say, a chisel. Diamond is the hardest substance known and has a melting temperature (under pressure) of over 3 500 °C.

- ☐ How does diamond differ from the covalent compounds we have met so far?
- It contains no discrete molecules, and its melting temperature is very high.

The absence of discrete molecules means that the C—C bonds must be broken if the structure is to be dismembered, and this accounts for the high melting temperature. As the C—C bonds consist of shared electron pairs, diamond is covalent, but it is not *molecular* covalent in the sense described in Section 6.6. We could argue the contrary only if we were prepared to

EXTENDED COVALENT
SUBSTANCE

ELECTRONEGATIVITY

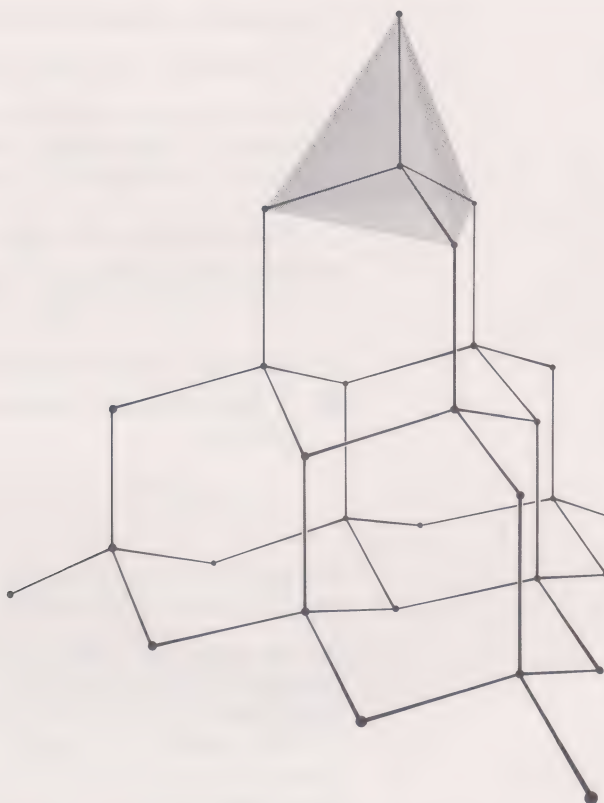


FIGURE 31 The structure of diamond. Each carbon atom is surrounded by four others located at the corners of a tetrahedron, as indicated by the shading. The length of the C—C bond is 154 pm.

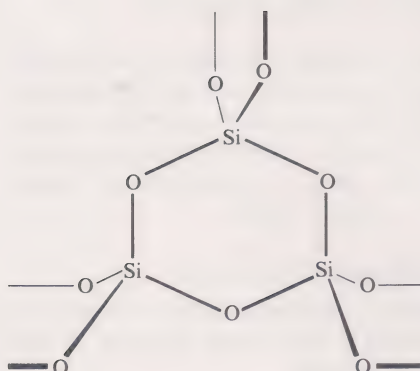


FIGURE 32 Simplified structure of quartz. The length of the Si—O bond is 161 pm.

concede that entire diamond crystals could be regarded as giant molecules. Instead, we shall describe diamond as an **extended covalent substance**.

You probably know that diamond is not the most common form of carbon. Another kind is called graphite, and its structure is discussed in Section 7.8.

The element silicon occurs in the same group of the Periodic Table as carbon, and it provides another well known example of an extended covalent substance. This is silica or silicon dioxide, SiO_2 , which resembles carbon dioxide, CO_2 , only in its formula. Carbon dioxide is a gas at room temperature and is present to the extent of 0.03% in air. It consists of discrete molecules, and in Section 7.4 you drew a Lewis structure for the molecule, which showed that it is held together by carbon–oxygen double bonds ($\text{O}=\text{C}=\text{O}$). The physical properties of SiO_2 are quite different from those of CO_2 . A fragment of the structure of quartz (one form of silica) is shown in Figure 32.

- ☐ Do the silicon and oxygen atoms have noble gas configurations?
- ☒ Yes. Each silicon forms four single electron-pair bonds directed towards the corners of a tetrahedron and attains the electronic configuration of argon; each oxygen forms two single bonds and attains the configuration of neon.

The overall ratio of silicon to oxygen atoms in silica is 1 : 2. The structure is a three-dimensional network of Si—O bonds: there are no discrete molecules. Like diamond, it is an extended, and not a molecular covalent substance. SiO_2 should be a solid, and if the Si—O bonds are strong, as in fact they are, the solid should be hard and melt at a high temperature. In fact SiO_2 (or silica) occurs as the mineral quartz or sand. As you probably know, quartz is very hard, and its melting temperature is 1710°C. A comparison of silica and carbon dioxide provides an excellent example of the effect of the bonding in a compound on its physical properties, and of the difference between extended and molecular covalent substances.

7.6 ELECTRONEGATIVITY

You have seen that when the atoms of non-metallic elements from the extreme right of the Period Table combine together, covalent substances are formed. However, combination of the atoms of a metallic element from the extreme left of the Table with atoms of a non-metallic element from the extreme right, yields ionic compounds. Consider, for example, the third Period, which runs from sodium to argon.



When atoms of chlorine combine with each other, gaseous covalent Cl_2 molecules are formed. But when chlorine atoms combine with sodium atoms, the ionic solid Na^+Cl^- is produced. Let us look at this contrast from an electronic point of view:



First comes the Lewis structure of the Cl_2 molecule. Then the ions in sodium chloride have been represented in a similar way. The chloride ion has the electronic configuration of argon, with eight outer electrons, and the electron transferred from the sodium atom is marked by a black dot. Following the convention of Section 7.4, the outer electrons are grouped in pairs. Notice that in both structures, the formation of a chemical bond involves the formation of a new electron pair in the outer electron configuration of chlorine. However, in Cl_2 , because the two atoms are identical, the electron pair must be equally shared between the two atoms: in NaCl by contrast, it resides completely on the resulting chloride ion. According to this picture, ionic and covalent bonding are just different aspects of a common process, because both involve the formation of electron pairs: *the difference between them lies only in the extent to which those electron pairs are shared between atoms.*

This link between ionic and covalent bonding can be strengthened by a concept called **electronegativity**. The electronegativity of an element is the power of an atom of the element to attract electrons to itself *when entering into chemical combination*. In the Cl_2 molecule, the two identical atoms have an equal appetite for electrons: their electronegativities are equal, so the electron pair is shared equally between the two atoms. Now consider sodium chloride.

☐ Which atom is the more electronegative, sodium or chlorine?

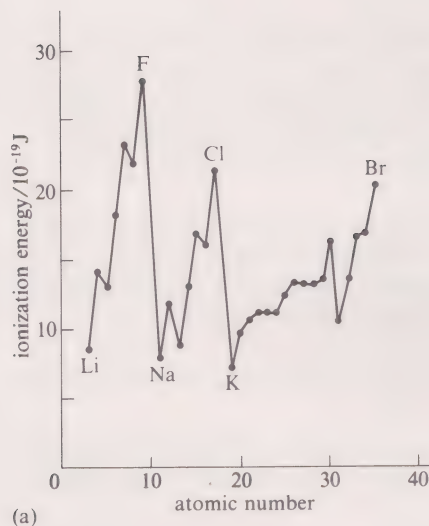
☒ Chlorine: in sodium chloride, the electron pair has been completely taken over by chlorine which forms a chloride ion. If you imagine that the sodium and chlorine atoms have competed for electrons, the chlorine atoms have won.

This argument suggests that the electronegativity of chlorine, near the end of the third Period, is greater than that of sodium at the beginning. A further hint that this is correct comes from the ionization energies of some elements in Figure 33a. If an element has a low ionization energy, then an electron is removed from its atom with relative ease, and this suggests that the electronegativity of the element should be low. By the converse argument, high electronegativities are associated with high ionization energies. Now look again at Figure 33a.

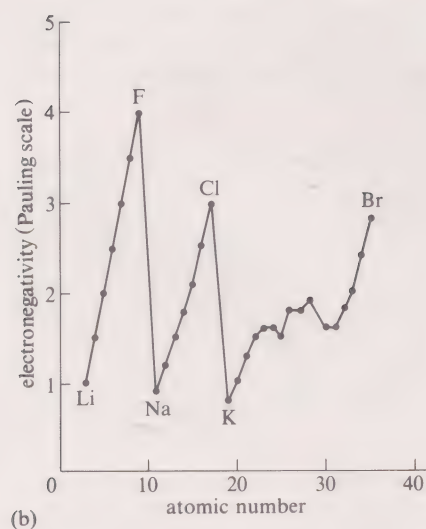
☐ Do the ionization energies of sodium and chlorine support these arguments?

☒ Yes; the ionization energy of chlorine, like its electronegativity, is the greater.

More advanced theoretical arguments suggest that electronegativity increases *steadily* across the third Period from sodium to chlorine. Such a change is apparent in Figure 33b, which shows the famous set of electro-



(a)



(b)

FIGURE 33 (a) Ionization energies and (b) electronegativities of the atoms of the chemical elements with atomic numbers 3 to 35. The values for the noble gases neon and argon, which form no chemical compounds, have been omitted.

negativities calculated by Linus Pauling, who won the Nobel Prize for chemistry in 1954. The overall similarity to the plot of ionization energies in Figure 33a is obvious. However, although the ionization energies do show a pronounced increase between sodium and chlorine, the increase is not smooth; it is broken by two hiccups. One reason for these inconsistencies is that electronegativity is a property of an atom *entering chemical combination*, whereas ionization energy is a property of a *free* atom. Nevertheless, despite such differences, ionization energies often provide a useful guide to trends in electronegativity. Consider, for example, how electronegativity might change within a Group in the Periodic Table.

- ☐ What change in electronegativity does Figure 33a suggest as one moves down Group VII from fluorine to bromine?
- As the ionization energy decreases steadily from fluorine to bromine, the electronegativity should do likewise.

Again this agrees with more advanced arguments embodied in Figure 33b. Indeed, within the Periodic Table in general, electronegativity usually increases from left to right across a Period, and decreases from the top to the bottom of a Group.

- ☐ Where in the Periodic Table are the most electronegative elements?
- At the top right-hand corner—the top of Groups and the end of Periods. Ignoring helium, neon and argon, which form no chemical compounds, the most electronegative elements are first, fluorine, followed by oxygen, chlorine and nitrogen.

These trends in electronegativity can help us to predict whether one substance is more likely to be ionic than another. From the trends in the formulae of the highest chlorides discussed in Section 4.1, magnesium and sulphur should form dichlorides, MgCl_2 and SCl_2 .

- ☐ In which of the two compounds is there the larger electronegativity difference between elements?
- In MgCl_2 ; electronegativity increases across a Period. Magnesium occurs near the beginning of the third Period; sulphur and chlorine occur together towards the end.
- ☐ Which of the two substances is more likely to be ionic?
- MgCl_2 ; the larger difference in electronegativity means that the chlorine is more likely to win control of electrons and form chloride ions. Sulphur and chlorine have high but similar electronegativities. SCl_2 is likely to be covalent.

As you know from Section 6.4, MgCl_2 is a colourless solid of high melting temperature (714°C) and the melt is a good electrical conductor. By contrast, SCl_2 is a non-conducting red liquid with a boiling temperature of only 59°C . These properties imply that, as predicted, MgCl_2 is ionic, and SCl_2 is covalent. Moreover, the predictions link up neatly with our bonding theories. The assertion that MgCl_2 should be ionic can be accommodated by the ionic formulation $\text{Mg}^{2+}(\text{Cl}^-)_2$, in which each ion has a noble gas structure. Conversely, the assertion that SCl_2 should be covalent can be accommodated by a Lewis structure in which sulphur and chlorine attain noble gas configurations (SAQ 30).

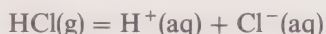
Earlier in this Section, chemical bond formation in Cl_2 and NaCl was regarded as formation of electron pairs: in covalent Cl_2 , each electron pair is equally shared between two atoms; in ionic NaCl , it belongs to chlorine, which is present as a chloride ion. These two cases are obviously extremes, and extremes in three senses. First, in one case the electronegativity difference between elements is zero, and in the other very large; secondly, in one case the electron pair is equally shared between two atoms, and in the other it is the property of just one of the two elements; finally, one case is covalent and the other ionic. Let us therefore examine one important intermediate case, that of hydrogen chloride, HCl . Assessments of the

electronegativity of hydrogen usually yield a value about halfway between the values for sodium and chlorine. So the electronegativity difference in HCl is about half that in NaCl.

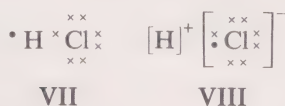
At normal temperatures and pressures, hydrogen chloride is a gas consisting of diatomic molecules, HCl. When cooled and liquefied, it does not conduct electricity. We therefore formulate it as a covalent compound:



Now when HCl gas is bubbled through water, a great deal of it dissolves, and aqueous ions are formed:



The resulting solution, hydrochloric acid, conducts electricity: thus HCl, a molecular covalent compound, has one property reminiscent of ionic substances. This can be related to an unequal sharing of the bonding electron pair between the hydrogen and chlorine atoms in the HCl molecule; chemists have their own way of representing this unequal sharing.



If a hydrogen and chlorine atom are juxtaposed *prior to any chemical bonding*, as in VII, the electron pair destined to form the chemical bond is split between both atoms: each atom possesses one of the two electrons, and neither H nor Cl has any net charge. If on the other hand, the electron pair becomes the sole property of chlorine, as in VIII, ions are formed in the combination H^+Cl^- . The charge distribution in the real situation lies somewhere between VII and VIII. The electron pair is not the sole property of chlorine, but because chlorine is considerably more electronegative than hydrogen, the sharing is unequal: the electron pair is attracted more towards chlorine than towards hydrogen.

Imagine therefore that the charge transfer from hydrogen to chlorine can vary *continuously* between nothing as in VII, and an entire electron as in VIII. Then the real situation can be represented by saying that in HCl molecules, the chlorine carries a partial negative charge, and the hydrogen carries an equal partial positive charge. These partial charges are symbolized as follows:



One indication of the presence of these partial charges in the molecule is that in water the charge transfer is completed, and HCl gas dissolves to give $\text{H}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ ions.

This then is a reminder that the ionic and covalent substances defined in Sections 6.4 and 6.6 are idealizations at the extremes of behaviour. Sometimes it may not be entirely easy to fit real substances into one of these two categories. The ideas developed in this Section imply that this may be especially so for binary compounds in which the electronegativity difference has intermediate values.

Such ideas dispose of a loose end from Section 6.4, which was concerned with the action of water as a solvent.

Assign partial charges to the atoms in the water molecule.

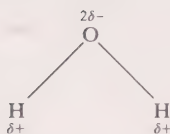


FIGURE 34 The charge distribution in the water molecule. Negative charge is concentrated at the oxygen atom; positive charge is concentrated around hydrogen. Notice that the water molecule is bent; you will learn more about the shapes of molecules in Units 17-18.

Oxygen, like chlorine, is one of the most electronegative elements. So oxygen in H_2O , like chlorine in HCl, carries a partial negative charge. The resulting charge distribution is shown in Figure 34. Note that because there are two hydrogen atoms, and because the total charge must be zero, the partial charge of oxygen is doubled.

In Section 6.4, the insolubility of NaCl in heptane was attributed to the strong attractive forces between oppositely charged ions in the solid. This

POLAR SOLVENT

NON-POLAR SOLVENT

METALLIC BONDING

METALS

ALLOY

NON-METAL

SEMI-METAL

SEMICONDUCTOR

raised a difficulty: why do these forces not also prevent NaCl dissolving in water?

In water, the Na^+ ions tend to surround themselves by the negative oxygen regions of the water molecules; in contrast, the Cl^- ions are surrounded by the positive hydrogen regions. In favourable circumstances, the attractive forces between ions and water molecules in the solution may outweigh those in the solid ionic substance, so the latter can dissolve.

Solvents, such as water, that consist of molecules within which there is substantial charge separation are called **polar solvents**, in contrast to **non-polar solvents**, such as heptane, which do not. Ionic substances can often dissolve in polar solvents to form conducting solutions. By contrast, in non-polar solvents, the interactions between the ions and the solvent molecules are too weak to allow dissolution to take place.

You have now seen that when atoms of high but similar electronegativity from the right-hand side of the Periodic Table bond together, covalent substances are formed. You have also seen that when these atoms of high electronegativity combine with atoms of low electronegativity at the extreme left of the Periodic Table, ionic compounds tend to be formed. But what happens when atoms of low but similar electronegativity on the left-hand side of the Periodic Table combine with each other?

7.7 METALLIC BONDING

At first sight, the arguments of Section 7.6 supply a ready answer to this question. The elements on the extreme left of the Periodic Table all have low electronegativities, so when they combine together, electronegativity differences will be small. Consequently, the result should be similar to the one observed when non-metallic atoms of *high* electronegativity bond together: shared electron-pair bonds and covalent substances. This however, is incorrect: electron sharing does take place, but in a new and interesting way.

Because all the atoms have low electronegativities, they are prepared to surrender electrons to other atoms, either by electron transfer or electron-pair sharing. However, low electronegativity also means that none of the atoms present will readily *take on* these electrons, either by forming a negative ion, or by accepting a share in electron-pair bonds. Consequently, a pool of free electrons is created, which is like hot money—they are passed quickly from hand to hand, and can find no permanent home! Within this pool resides an array of positive ions formed from the atoms that supplied it (Figure 35). Ultimately, each atom shares its bonding electron(s) with every other atom in the crystal. This is a simple model of **metallic bonding**, a kind of binding you have not met before. *When the atoms of elements on the left of the Periodic Table combine together, metallic substances (metals) are formed.*

Consider a specific example. When sodium atoms combine with one another, sodium metal is formed.

- ☐ In sodium metal, how many electrons will each sodium atom contribute to the pool of free electrons?
- ☒ One; by so doing, each atom forms an Na^+ ion with the noble gas structure of neon.

According to this model, therefore, sodium metal consists of an array of Na^+ ions immersed in a pool of free electrons.

- ☐ How is the metal held together?
- ☒ By the electrical attraction between the positive ions, and the intervening, negatively charged electrons.

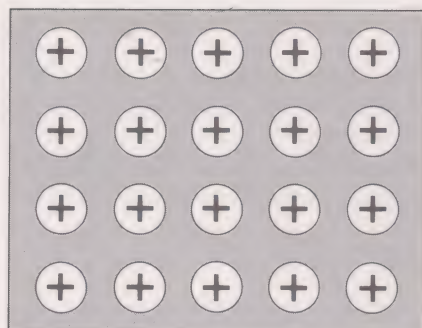


FIGURE 35 A simple model of metallic bonding: in metallic elements and alloys, an array of positive ions is steeped in a pool of negatively charged free electrons.

Because there is only one bonding electron per metal atom in sodium, the bonding is quite weak, and the melting point is low (98°C). With magnesium, the next element in the Period, the ion with a noble gas structure is Mg^{2+} . This double positive charge now interacts with the negative charge of the two free electrons per metal atom. The bonding is therefore stronger, and the melting point higher (650°C).

You will be familiar with the distinctive properties of metals from everyday contact with substances such as iron, aluminium, copper, silver and tin. **Metals** often have a lustrous appearance, and are good conductors of heat and electricity. The free electrons, which roam throughout the metal structure, account for the electrical conductivity. When a voltage is applied across two points on a piece of metal, the electron motion becomes less random, there is an overall movement of electrons between the two points, and an electric current flows.

So far, the metals discussed in this Section have been composed of atoms of the same element. When atoms of different metallic elements combine together, and a metallic substance is formed, the substance is called an **alloy**. Alloys are immensely important because they often have properties that are more desirable than those of the metallic elements from which the alloy was made. Bronze, for example, is much tougher than its component metals, copper and tin. Alloys are easily accommodated by the free electron model of Figure 35; in an alloy of magnesium and aluminium, for instance, the array of positive ions consists of Mg^{2+} and Al^{3+} , and the free electron pool contains two electrons from each magnesium atom, and three from each aluminium atom.

7.8 THE BOUNDARY BETWEEN METALLIC AND NON-METALLIC ELEMENTS

In Section 4.4, the distribution of metals, semi-metals and non-metals was used to derive a long form of the Periodic Table. Now you know how metals are defined, the term **non-metal** should be self-explanatory. **Semi-metals** fall between the two, both in their position in Figure 13 and in their properties.

Section 7.7 asserts that in metals such as sodium, the bonding electrons roam freely through the structure; Section 7.4 states that in non-metals such as chlorine or diamond, the bonding electrons are localized in covalent bonds between atoms. In semi-metals, a *very small proportion* of the electrons in covalent bonds become free like the bonding electrons in a metal. This happens, for example, in solid silicon and germanium, which are Group IV elements like carbon and have the diamond structure of Figure 31. The small concentration of free electrons causes semi-metals to fall between metals and non-metals as regards appearance and electrical conductivity. Some semi-metals, such as boron, have a distinctly unmetallic look; others, like antimony, have a decidedly metallic appearance. However all conduct electricity, although not as readily as metals. They are members of the group of substances known as **semiconductors**, and their conductivity is much affected by the presence of trace impurities.

Finally, let us go back to carbon, whose non-metallic character is evident in the properties of the covalently bound structure of diamond (Section 7.5). Although a non-metal, carbon lies close to the boundary between metals and non-metals, and one remarkable sign of this position is the structure of graphite, the more common of the two forms of carbon. Among the chemical elements, this structure is unique: it is held together by a *combination* of covalent and metallic bonding.

Graphite is familiar to you as soot, or as the so-called 'lead' in pencils. Unlike diamond, it is quite soft, and is used as a lubricant. Even more surprisingly, it is a good conductor of electricity. The crystal structure of graphite (Figure 36) shows that it consists of sheets of carbon atoms. Each atom is bound to three others in the same sheet. Carbon has four outer

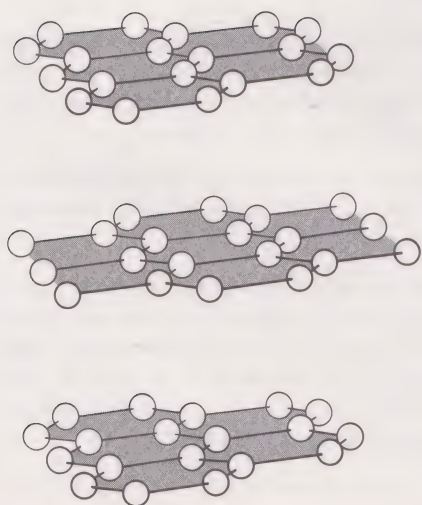


FIGURE 36 The structure of graphite showing parallel sheets of carbon atoms. The C—C bond length within the sheets is 142 pm, and the separation of the sheets is 335 pm.

electrons ($2s^2 2p^2$); in graphite, each carbon atom shares three of these with three other carbon atoms in the same sheet by forming three covalent bonds. The fourth electron is mobile, just as the bonding electrons in a metal are mobile; it binds carbon atoms within its sheet together more strongly by contributing to a pool of electrons concentrated around the plane of the sheet.

- ☐ Can you see why graphite should be both soft and a good lubricant?
- The bonding is concentrated within the sheets. One sheet is bound to another only weakly and they are separated by relatively large distances. Consequently, comparatively small forces will cause sheets to slip over each other.

This easy slippage explains the lubricant properties of graphite and the ease with which small flakes can be detached.

- ☐ Suppose you had a cube of graphite cut from a single crystal. Would the electrical conductivity be the same in all directions?
- No. The mobile electrons move freely *within* the sheets of carbon atoms but not *through* them. Consequently, within the planes, the electrical conductivity is about 1 000 times that of the conductivity at right angles to them.

It is this conductivity that was exploited when you used graphite electrodes during Experiments 4 and 5.

SUMMARY OF SECTION 7

- 1 Many substances are formed by atoms bonding together in order to attain the highly stable electronic configurations of the noble gases.
- 2 Three main types of chemical bonding have been discussed here:
 - (i) Ionic bonding, in which ions with noble gas configurations are formed by electron transfer;
 - (ii) Covalent bonding, in which atoms achieve noble gas configurations by sharing electron pairs;
 - (iii) Metallic bonding, in which positive ions with noble gas configurations are held together by a pool of free electrons.
- 3 These three different kinds of bonding give rise to the distinctive properties of ionic, covalent and metallic substances.
- 4 Whether a substance is ionic, covalent or metallic is strongly influenced by the electronegativity of the atoms of which it is composed. In general, electronegativity increases from left to right across Periods of the Periodic Table, and decreases down Groups from the top to the bottom.
- 5 This variation means that the non-metallic elements on the extreme right of the Periodic Table have high electronegativities; metallic elements at the extreme left have low electronegativities.
- 6 When non-metallic elements combine with themselves, or with each other to form binary compounds, their high but similar electronegativities result in the formation of shared electron-pair bonds. In other words, they form covalent substances. In many, but not all cases these substances can be represented by Lewis structures in which each non-metallic atom attains the electronic configuration of the noble gas at the end of its Period.
- 7 When non-metallic elements from the extreme right of the Periodic Table form binary compounds with metallic elements from the extreme left, the large difference in electronegativity tends to generate ionic compounds. Such compounds can often be represented as assemblies of ions in which the metallic element has formed a positive ion with the electronic configuration of the preceding noble gas, and the non-metallic element has formed a negative ion with the electronic configuration of the following noble gas.

8 When elements from the left of the Periodic Table combine with themselves, or with each other, their low electronegativities generate assemblies of positive ions within a pool of free electrons. These free electrons account for the metallic properties of such elements, and also of the substances that they form by combination which are called alloys.

When you do SAQs 27–35, you will find it helpful to refer to the condensed Periodic Table in Figure 37. This shows the Group number of the element, and the outer electronic configuration of the atoms. It also points out the overall variation in electronegativity within the Periodic Table.

increasing electronegativity →

I	II	III	IV	V	VI	VII	0
s^1	s^2	s^2p^1	s^2p^2	s^2p^3	s^2p^4	s^2p^5	s^2p^6
							He
Li			C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca		Ge			Br	Kr
Rb			Sn			I	
Cs							

↓ decreasing electronegativity

FIGURE 37 A fragment of the Periodic Table of Figure 17 showing the positions of the chemical elements in SAQs 27–35, the outer electronic configurations for the Groups, and the overall variation in electronegativity. Note that the transition elements and the lanthanides have been removed: the resulting gap is marked by dashed lines.

SAQ 27 Potassium and magnesium react with sulphur to form ionic sulphides. What is the charge of the sulphide ion in these compounds? Use your answer to predict the formulae of potassium sulphide and magnesium sulphide.

SAQ 28 Lithium and calcium react with nitrogen to form ionic nitrides. What is the charge of the nitride ion in these compounds? Predict the formulae of lithium nitride and calcium nitride.

SAQ 29 In the following list of elements, the most common valencies are given in brackets: carbon (4), oxygen (2), sulphur (2), fluorine (1) and chlorine (1). The following covalent compounds contain discrete molecules with the formulae given in brackets: dichlorine monoxide (Cl_2O), carbon tetrafluoride (CF_4), carbon disulphide (CS_2), and the former war gas, phosgene (COCl_2). Draw a diagram for each molecule in which bonds are represented by lines.

SAQ 30 Oxygen gas, sulphur dichloride and ammonia contain discrete molecules with the formulae O_2 , SCl_2 and NH_3 , respectively. Draw a Lewis structure for each molecule. What noble gas structure is attained by each atom in the molecules?

SAQ 31 When ammonia gas dissolves in water, small amounts of the ion NH_4^+ (aq) are formed. Build up a Lewis structure for NH_4^+ by bonding an N^+ ion to four hydrogen atoms.

SAQ 32 Nitrogen forms the compounds nitrosyl chloride (NOCl) and hydrazine (N_2H_4), which consist of discrete molecules. For each compound, draw diagrams of the molecules in which bonds are represented by lines, and each kind of atom has its common valency: nitrogen (3), oxygen (2), chlorine (1) and hydrogen (1). Then, for each case, draw the corresponding Lewis structure.

SAQ 33 Consider the following pairs of fluorides: (i) AlF_3 and PF_3 ; (ii) CF_4 and SnF_4 . One member of each pair is classified as an ionic substance,

the other as a covalent substance. State which is which, expressing your reasons in terms of electronegativity.

SAQ 34 Consider the compounds IBr , CaCl_2 and CaMg_2 . One is ionic, one is covalent and one is metallic. Identify which is which, and then match each compound to one of the three descriptions (i)–(iii) below:

- (i) White solid that melts at 782°C . It is a poor conductor of electricity in the solid state, but a good one when melted or dissolved in water.
- (ii) Brown-black solid that melts at 41°C to give a liquid with low electrical conductivity.
- (iii) Silvery looking solid that melts at 720°C . Whether solid or molten, it is an excellent conductor of electricity.

SAQ 35 Examine statements (a)–(c) below, which describe properties of carbon tetrachloride, CCl_4 , fluorine oxide, F_2O , and rubidium oxide, Rb_2O . These substances are either ionic or covalent. Where you think a substance is ionic, assign charges to each ion. Where you think a substance is covalent, write a Lewis structure for it.

- (a) CCl_4 is a liquid at room temperature and does not conduct electricity; it boils at 77°C .
- (b) F_2O is a gas at room temperature.
- (c) Rb_2O is a solid with a high melting temperature. The structure is such that each rubidium is surrounded by four equidistant oxygens and each oxygen by eight equidistant rubidiums.

8 SUMMARY OF THE CHEMISTRY OF THE ALKALI METALS AND HALOGENS

In these Units, the groups in the Periodic Table that received most attention were the alkali metals of Group I, and the halogens of Group VII. Here is a brief summary of the chemistry of those elements.

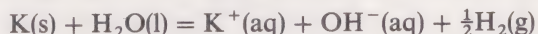
8.1 GROUP I—THE ALKALI METALS

The elements concerned are lithium, sodium, potassium, rubidium and caesium. They lie on the extreme left of the Periodic Table, and the atoms have outer electronic configurations of the type ns^1 . These configurations, combined with their low electronegativities, mean that the chemistry of the elements is dominated by the formation of singly charged positive ions that have the electronic configuration of the preceding noble gas.

For example, when the alkali metals combine with elements on the extreme right of the Periodic Table, such as oxygen or the halogens, the large electronegativity differences lead to the formation of ionic oxides and halides, such as $(\text{Li}^+)_2\text{O}^{2-}$ and K^+Cl^- , in which each ion has a noble gas configuration. These structures have the properties expected of ionic compounds. Thus, the halides are solids with high melting temperatures, and their melts conduct electricity. Most of the halides have the sodium chloride structure (Figure 25), in which each ion is surrounded by others of opposite charge.

Many other alkali metal compounds are ionic substances containing the singly charged cation with a noble gas configuration. This is true, for example, of all compounds put together by combining any alkali metal cation with any anion from Table 5. All such substances are white solids, which usually dissolve in, or react with water to give solutions containing the aqueous cations, $\text{Li}^+(\text{aq})$, $\text{Na}^+(\text{aq})$, $\text{K}^+(\text{aq})$, $\text{Rb}^+(\text{aq})$ or $\text{Cs}^+(\text{aq})$. These

ions are also formed during the violent reactions of the metals with water which you saw in the TV programme 'Elements organized', for example:



The singly charged cations also play a part in models of the bonding in the metals. Their presence means that there is only one electron per atom in the free electron pool, so the bonding is relatively weak, and the melting temperatures low. Sodium, for example, melts at only 98 °C, and caesium, as you saw in the TV programme, melts in the hand.

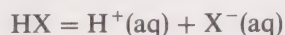
8.2 GROUP VII—THE HALOGENS

The elements concerned are fluorine, chlorine, bromine and iodine. They lie on the extreme right of the Periodic Table and the atoms have outer electronic configurations of the type ns^2np^5 . These configurations, combined with high electronegativities, mean that much of halogen chemistry is dominated by the acquisition of an electron by the atoms to form the electronic configuration of the subsequent noble gas. This can be done in two ways:

- (i) When a halogen combines with other electronegative non-metallic elements, the noble gas configuration can be achieved through the sharing of electron pairs in covalent bonds. This happens in the halogen elements, which consist of diatomic molecules and, as you saw in Experiment 5, have properties characteristic of molecular covalent substances: fluorine and chlorine are pale-yellow and greenish-yellow gases, bromine is a red liquid, and iodine a volatile purple solid. Many other instances of volatile molecular covalent halides are given in Section 7, e.g. SCl_2 , CCl_4 and NCl_3 .
- (ii) When a halogen combines with metallic elements of low electronegativity from the extreme left of the Periodic Table, the noble gas configuration can be attained by formation of a singly charged negative ion. This yields ionic compounds like the alkali metal halides discussed in Section 8.1. Other examples discussed in Section 7 included $\text{Mg}^{2+}(\text{Cl}^-)_2$ and $\text{Al}^{3+}(\text{F}^-)_3$. Such substances are solids, have high melting temperatures, and conduct electricity in the molten state.

SAQ 36 Hydrogen is a difficult element to place in the Periodic Table, but if a choice has to be made, chemists usually settle for Group I or Group VII. This SAQ gives you the opportunity of using Section 8 to take your own decision.

Consider the following properties of hydrogen: its highest oxide is water, H_2O , and it forms a series of gaseous halides, HF, HCl, HBr and HI, which dissolve in water to produce ions:



The element itself is a gas consisting of diatomic molecules, H_2 , and it combines with the alkali metals and Group II metals to give hydrides such as KH and CaH_2 . Molten CaH_2 conducts electricity. The hydrogen atom has the electronic configuration $1s^1$.

In Figure 17 hydrogen has been left 'hanging in the air'. If you were forced to put it into Group I or Group VII, which position would you choose?

9 TV NOTES: ELEMENTS DISCOVERED

There are more than a hundred known chemical elements; some have been known since antiquity, and others, which can only be produced in nuclear reactions, have been discovered in recent years. These elements are the substances from which all matter is formed. Except in nuclear reactions the elements cannot be transformed from one into another.

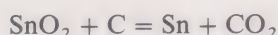
In this programme we examined how the number of known elements has changed over the years, and looked at various episodes in this history. We picked out the relationship between the available technology and the elements that were discovered at various times, in order to highlight the interdependence of science and technology. The episodes of discovery are as follows:

The ancient elements

We examined how the elements that are used to make copper and tin were produced from their ore. These two metals are melted together to give the alloy bronze. Many of the ancient metals were prepared by smelting, heating an ore in a furnace fired by charcoal. The green ore of copper (malachite) is decomposed at the temperature of the furnace to give the black copper(II) oxide. In the furnace this oxide reacts with carbon to form the metal:



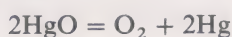
Similarly, the oxide of tin, cassiterite, forms metallic tin:



The gases of the air

The development of glassware to handle gases assisted the discovery that the air is composed largely of two elements: nitrogen and oxygen. When a candle is burned in air, oxygen reacts with the wax, but nitrogen does not react.

Oxygen is produced when mercuric oxide is heated by the Sun's rays.



The halogens

Chlorine, a gas, was discovered at about the same time as oxygen and nitrogen. It is formed in the reaction of manganese dioxide with hydrochloric acid:



Hydrochloric acid is made from sodium chloride, originally salt from the sea. You saw how bromine and iodine also originated from the sea, bromine from seawater and iodine from seaweed.

The alkali metals

The discovery of electrolysis led to other new elements. In the early nineteenth century Sir Humphry Davy prepared the alkali metals and alkaline earth metals by electrolysis. You saw how he made potassium and calcium.

Flame spectroscopy

The invention of the bunsen burner and spectroscopy in 1860 gave rise to a large number of new discoveries. By now you should know that only a little of a substance is needed to analyse its flame spectrum. Consequently, rare elements long hidden by their low concentrations were suddenly and dramatically revealed.

The lanthanides

In 1787 a young Swedish mineralogist discovered an unusual ore in a quarry near Ytterby in Sweden. This ore was later found to contain more than ten chemically very similar elements, the lanthanides. Since the elements are chemically so similar, they were difficult to separate. However, each element has its characteristic spectrum, so flame spectroscopy was used to identify each one.

The noble gases

Atomic spectroscopy also revealed a new element in the Sun—helium. This turned out, along with several other colourless and inert gases, to be present in the Earth's atmosphere. At the end of the 19th century these elements were separated by distillation at low temperatures, a technique made available by the liquefaction of air.

The artificial elements

The most recently discovered elements are those that have to be made artificially, for example plutonium, either in a nuclear reactor or by bombarding lighter elements with fast particles (Units 11–12). The alchemists' dream of being able to transmute elements has been realized (Figure 38).

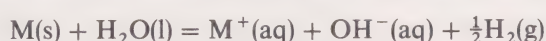


FIGURE 38 'Today I'd be happy just to turn gold to lead.'

10 TV NOTES: ELEMENTS ORGANIZED—THE PERIODIC TABLE

This programme covers and provides experimental support for the ideas in Section 4.

The programme opened with a series of shots showing the great variety in the behaviour of the chemical elements. It then went on to show how MendeléeV systematized much of this variety by means of his Periodic Table. The meanings of the terms *Group* and *Period* were explained, and the similarities between elements of the same Group were demonstrated by studying the physical properties of the noble gases (Group 0) and the chemical reactions of the alkali metals (Group IA). You were shown the rapid corrosion of the alkali metals in air, and the reaction with water:



Trends across a Period were illustrated by studying the reactions of the elements of the neon-chlorine row in Mendelée's Table with fluorine and with oxygen. In both cases, as one moves across the Period, there is a regular change in the formulae of the highest fluoride and the highest oxide. If one writes the formulae of the highest fluoride and highest oxide as MF_n and M_2O_n , n changes from 0 to 7 as one moves from neon to chlorine, except in the case of the fluoride of chlorine. The importance of chemical formulae in establishing the common characteristics of elements in the same Group were then further emphasized. This was done by comparing the formulae of the combustion products of diamond and silicon, and contrasting their physical and structural properties.

The weaknesses of Mendelée's Table were then highlighted. The reactions with water of Group IA (the alkali metals) were contrasted with those of Group IB (copper, silver and gold). Finally, the distribution of metals, semi-metals and non-metals was used to convert Mendelée's Periodic Table into the modern long form. This was done by repeating the exercise of Section 4.4 on animated film.

II SUMMARY OF UNITS 13–14

Units 13–14 contain the fundamentals of chemistry. In Section 2, you were shown how chemical elements that you met in Units 11–12 can combine to form compounds. Here was chemistry's way of looking at the world: all matter consists of either chemical elements, or some combination of them.

In Sections 3 and 3.1, you encountered chemical compounds in which the atoms of the chemical elements are combined in simple numerical ratios. These ratios were expressed by chemical formulae which, in Section 3.2, were used to describe chemical changes through chemical equations. You could then imagine experiments in which just one chemical element, such as chlorine, was combined with each of the other elements in turn. With some elements, such as hydrogen and sodium, the atomic ratios then turn out to be the same (HCl and NaCl); in others, such as oxygen and nitrogen, they are different (OCl_2 and NCl_3).

We then looked for regularities in these formulae. First, in Section 3.3, we assigned valencies to some of the elements. Secondly, in Sections 4 to 4.2, we showed that if the elements were arranged in order of atomic number, there was a tendency for the same numerical ratios to crop up at regular intervals. This led us to Mendelée's short Periodic Table.

In Sections 4.3 and 4.4, weaknesses were exposed in this Table, and by shifting attention away from chemical formulae and asking which elements were metals and which non-metals, we created a long Periodic Table that was free of ad hoc contrivances. In Section 5, the virtues of this new Table were confirmed by showing that it mirrored the periodicity in the electronic configurations of atoms.

Finally, by studying chemical bonding, we sought an explanation of the different atomic ratios in which the elements combine. First, the distinction between ionic and covalent substances was set up in Section 6. Then, in Section 7, many chemical formulae were explained by the tendency of elements to acquire noble gas electronic configurations. In ionic substances this is done by generating ions; in covalent substances through the formation of shared-electron-pair bonds; in metallic substances by the generation of positive ions and a pool of free electrons. Whether substances are ionic, covalent or metallic is strongly influenced by the electronegativities of the constituent elements. In Section 8, these principles were illustrated in a brief summary of the chemistry of the alkali metals and the halogens.

REVISION SAQs

These SAQs are *not* part of the two weeks' work allocated to these two Units. They are meant to help you later when you are revising for the examination.

SAQ 37 A litre of water (H_2O) has a mass of 1 000 g. How many moles of water are contained in one litre?

SAQ 38 A one pence copper coin has a mass of 3.5 g. How many one pence coins do you need to make a mole of copper? How many atoms are contained in one coin?

SAQ 39 Gaseous nitrogen N_2 makes up about 80% of air and it has a density of about 1.22 kg m^{-3} under ordinary conditions at the Earth's surface. What is the volume of a mole of nitrogen (N_2 molecules) under these conditions?

SAQ 40 1.00 g of phosphorus (P) reacts completely with bromine (Br_2) to produce a yellow solid that contains 12.90 g of bromine. What is the empirical formula of this yellow solid?

SAQ 41 When a solution containing 5.00 g of bromine (Br_2) is heated with 5.00 g of antimony (Sb), the bromine reacts completely, a white compound is formed and 2.46 g of antimony remain. What is the empirical formula of the white product?

SAQ 42 Sulphur (S) burns spontaneously in the gas fluorine (F_2) to produce a colourless gas. If 1.00 g of sulphur gives 4.56 g of product, what is the empirical formula of the product?

SAQ 43 If the valency of the elements fluorine and bromine is taken to be one, what is the valency of each of the other elements in the binary compounds described in SAQs 40, 41 and 42?

SAQ 44 What is the valency of iron in the compound Fe_2O_3 , assuming that oxygen has a valency of two?

SAQ 45 What is the formula of the binary compound formed between silver (with valency one) and oxygen (with valency two)?

SAQ 46 Write balanced equations to show what happens when the following electrolytes are dissolved in water: sodium carbonate, Na_2CO_3 ; ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$; iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3$; nickel sulphate, NiSO_4 .

SAQ 47 When aqueous solutions containing the following pairs of ions are mixed, the ions combine to form insoluble solid compounds. Write balanced equations to represent the formation of these insoluble substances.

(a) Pb^{2+} and SO_4^{2-}

(b) Al^{3+} and PO_4^{3-}

(c) Ag^+ and S^{2-}

SAQ 48 Write a balanced chemical equation to represent the reaction of solid phosphorus with liquid bromine to produce the yellow solid PBr_5 . Indicate the phases of the substances in the equation.

SAQ 49 Write a balanced chemical equation that includes phases to represent the reaction of sulphur with fluorine to produce the colourless gas SF_6 .

SAQ 50 (A harder question on balancing equations) The gas butane (molecular formula C_4H_{10}) is used as a fuel in gas cylinders. It burns in air

to produce only carbon dioxide and water. Write a balanced chemical equation to represent the combustion of butane.

SAQ 51 The substance PCl_3 (phosphorus trichloride) reacts with water to produce only H_3PO_3 (phosphorous acid) and HCl . Represent this reaction by an equation.

SAQ 52 Write balanced chemical equations to show which aqueous ions are produced when the following solid substances dissolve in water:

- (i) sodium hydroxide, NaOH
- (ii) zinc nitrate, $\text{Zn}(\text{NO}_3)_2$
- (iii) calcium nitrate, $\text{Ca}(\text{NO}_3)_2$
- (iv) ammonium chloride, NH_4Cl
- (v) iron(II) chloride, FeCl_2

SAQ 53 Write down the electronic structures of the atoms of elements with atomic numbers 34 and 38. In which Groups of the Periodic Table would you place these elements? What are the formulae of the highest oxides and hydrides that you would expect these elements to form? What is the formula of the binary compound that you would expect to be formed between elements 34 and 38?

SAQ 54 Which of the compounds in SAQ 53 would you expect to be covalent and which ionic?

SAQ 55 This question concerns elements X and Y, whose properties are given in (i) and (ii) below. In which Groups of Mendelée's Periodic Table do elements X and Y lie? What types of element are X and Y? What can be inferred about their electronic structure?

(i) At room temperature, a solid element X is a poor conductor of electricity. It forms a single chloride XCl_3 and a single hydride XH_3 . XCl_3 is a colourless liquid, which boils at 200°C and does not conduct electricity.

(ii) An element Y forms a series of oxides with the empirical formulae YO (a green solid), Y_3O_4 (a black solid), Y_2O_3 (a black solid), YO_2 (a black solid), YO_3 (a red solid) and Y_2O_7 (a red liquid).

SAQ 56 The elements magnesium and aluminium each react with phosphorus when heated to form binary compounds called phosphides. If these compounds are ionic, what charge will the ions have in each compound? What is the formula of each of these compounds?

SAQ 57 The substances H_2Se , Br_2 and PCl_3 each exist as covalent molecules. Draw a Lewis structure for each of them.

APPENDIX 1 Relative atomic masses* and atomic numbers of the elements

Element	Symbol	Atomic number	Relative atomic mass	Element	Symbol	Atomic number	Relative atomic mass
actinium	Ac	89	227	mercury	Hg	80	201
aluminium	Al	13	27.0	molybdenum	Mo	42	95.9
americium	Am	95	243	neodymium	Nd	60	144
antimony	Sb	51	122	neon	Ne	10	20.2
argon	Ar	18	39.9	neptunium	Np	93	237
arsenic	As	33	74.9	nickel	Ni	28	58.7
astatine	At	85	210	niobium	Nb	41	92.9
barium	Ba	56	137	nitrogen	N	7	14.0
berkelium	Bk	97	247	nobelium	No	102	254
beryllium	Be	4	9.01	osmium	Os	76	190
bismuth	Bi	83	209	oxygen	O	8	16.0
boron	B	5	10.8	palladium	Pd	46	106
bromine	Br	35	79.9	phosphorus	P	15	31.0
cadmium	Cd	48	112	platinum	Pt	78	195
caesium	Cs	55	133	plutonium	Pu	94	242
calcium	Ca	20	40.1	polonium	Po	84	210
californium	Cf	98	251	potassium	K	19	39.1
carbon	C	6	12.0	praseodymium	Pr	59	141
cerium	Ce	58	140	promethium	Pm	61	147
chlorine	Cl	17	35.5	protactinium	Pa	91	231
chromium	Cr	24	52.0	radium	Ra	88	226
cobalt	Co	27	58.9	radon	Rn	86	222
copper	Cu	29	63.5	rhenium	Re	75	186
curium	Cm	96	247	rhodium	Rh	45	103
dysprosium	Dy	66	163	rubidium	Rb	37	85.5
einsteinium	Es	99	254	ruthenium	Ru	44	101
erbium	Er	68	167	samarium	Sm	62	150
europium	Eu	63	152	scandium	Sc	21	45.0
fermium	Fm	100	253	selenium	Se	34	79.0
fluorine	F	9	19.0	silicon	Si	14	28.1
francium	Fr	87	223	silver	Ag	47	108
gadolinium	Gd	64	157	sodium	Na	11	23.0
gallium	Ga	31	69.7	strontium	Sr	38	87.6
germanium	Ge	32	72.6	sulphur	S	16	32.1
gold	Au	79	197	tantalum	Ta	73	181
hafnium	Hf	72	178	technetium	Tc	43	98.9
helium	He	2	4.00	tellurium	Te	52	128
holmium	Ho	67	165	terbium	Tb	65	159
hydrogen	H	1	1.01	thallium	Tl	81	204
indium	In	49	115	thorium	Th	90	232
iodine	I	53	127	thulium	Tm	69	169
iridium	Ir	77	192	tin	Sn	50	119
iron	Fe	26	55.8	titanium	Ti	22	47.9
krypton	Kr	36	83.8	tungsten	W	74	184
lanthanum	La	57	139	uranium	U	92	238
lawrencium	Lr	103	257	vanadium	V	23	50.9
lead	Pb	82	207	xenon	Xe	54	131
lithium	Li	3	6.94	ytterbium	Yb	70	173
lutetium	Lu	71	175	yttrium	Y	39	88.9
magnesium	Mg	12	24.3	zinc	Zn	30	65.4
manganese	Mn	25	54.9	zirconium	Zr	40	91.2
mendelevium	Md	101	256				

* To three significant figures.

OBJECTIVES FOR UNITS 13–14

After you have worked through these two Units you should be able to:

- 1 Explain the meaning of, and use correctly, all the terms identified by bold type in the text.
- 2 State and apply the conservation laws for chemical reactions. (*ITQs 1 and 3, SAQs 1–5 and 40–42*)
- 3 Use chemical symbols to represent empirical formulae, molecular formulae, ionic formulae and the phases of substances. (*Nearly all ITQs and SAQs*)
- 4 Perform an experiment to determine the empirical formula of a substance. (*Experiment 2*)
- 5 Calculate the formula of a compound from its chemical composition. (*ITQs 1, 3 and 5, SAQs 3–5 and 40–42*)
- 6 Apply Avogadro's law to observations on reactions of gases. (*SAQs 6 and 39*)
- 7 Determine the valency of an element in a simple compound, given the formula of that compound; and deduce the formula of a compound from the valencies of the elements that it contains (*SAQs 11–13, 15*)
- 8 Balance chemical equations. (*ITQ 2, SAQs 8–10, 14, 46–53*)
- 9 Perform calculations involving moles of substances and molar masses. (*ITQ 5, SAQs 7, 37–39*)
- 10 Given information about the properties of an unknown element, notably the formulae of halides, hydrides and oxides, use a Periodic Table to identify either the element, or a Group of which the element is a member. (*SAQs 17–20, 36, 55*)
- 11 Given the atomic number of an element, and the appropriate sequence of s, p, d and f subshells in order of increasing energy, write down the electronic configuration of the free atom of the element. (*SAQs 19–21, 55*)
- 12 Given the name of a simple compound, and the ions that it forms when it dissolves in water, write down both the chemical formula of the compound, and a balanced equation for the dissolution reaction. (*SAQs 22–24*).
- 13 Distinguish ionic, covalent and metallic substances given their appropriate structural and physical properties. (*SAQs 25, 26, 34–36, 46, 47, 52*)
- 14 Given the formula of a simple molecular covalent compound, and the valencies of the constituent elements, represent the molecule by a diagram in which chemical bonds are drawn as lines. (*ITQ 6, SAQs 29, 30, 56*)
- 15 Write down possible symbols for the monatomic ions of typical elements by assuming that the element tends to attain the electronic configuration of the nearest noble gas. (*SAQs 27, 28, 35, 36, 53*)
- 16 Write down Lewis structures for simple covalent compounds. (*SAQs 30–32, 57*)
- 17 Given a Periodic Table and/or a knowledge of the electronegativity trends within it, make an assessment of whether a given element or binary compound is likely to be ionic, covalent or metallic. (*SAQs 33–35, 54*)

ITQ ANSWERS AND COMMENTS

ITQ 1 Fe_2O_3 .

The chemical composition of the compound is calculated as follows:

$$m(\text{Fe}) = 4.00 \text{ g}$$

$$\begin{aligned} m(\text{O}) &= (5.72 - 4.00) \text{ g} \\ &= 1.72 \text{ g} \end{aligned}$$

The numbers of atoms in the sample of the compound are:

$$\begin{aligned} n(\text{Fe}) &= \frac{4.00 \text{ g}}{92.7 \times 10^{-24} \text{ g}} \\ &= 4.31 \times 10^{22} \end{aligned}$$

$$\begin{aligned} n(\text{O}) &= \frac{1.72 \text{ g}}{26.6 \times 10^{-24} \text{ g}} \\ &= 6.47 \times 10^{22} \end{aligned}$$

The ratio of atoms is:

$$\begin{aligned} \frac{n(\text{O})}{n(\text{Fe})} &= \frac{6.47 \times 10^{22}}{4.31 \times 10^{22}} \\ &= 1.50 \end{aligned}$$

Expressed as a ratio of integers

$$\frac{n(\text{O})}{n(\text{Fe})} = \frac{3}{2}$$

The empirical formula is thus Fe_2O_3 . [The red compound is an oxide of iron known as iron(III) oxide, rust.]

ITQ 2 (a) The amount of helium in 100 g is:

$$\frac{100 \text{ g}}{4.00 \text{ g mol}^{-1}} = 25 \text{ mol}$$

(b) The amount of iron in 100 g is:

$$\frac{100 \text{ g}}{55.8 \text{ g mol}^{-1}} = 1.79 \text{ mol}$$

ITQ 3 The empirical formula is CO_2 .
The number of moles of carbon atoms is

$$\frac{\text{mass of carbon}}{\text{molar mass of carbon}} = \frac{24.02 \text{ g}}{12.0 \text{ g mol}^{-1}}$$

$$= 2.00 \text{ moles of carbon atoms}$$

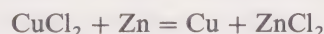
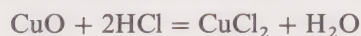
The number of moles of oxygen atoms is

$$\frac{\text{mass of oxygen}}{\text{molar mass of oxygen}} = \frac{64.0 \text{ g}}{16.0 \text{ g mol}^{-1}}$$

$$= 4.00 \text{ moles of oxygen atoms}$$

So two moles of carbon atoms react with four moles of oxygen atoms. In the product, C and O atoms are combined in the ratio 2:4. The empirical formula employs this ratio reduced to its simplest integral value, 1:2. So we can conclude that the empirical formula of the product is CO_2 . This is pronounced 'C O two'.

ITQ 4 The two balanced equations are as follows:



ITQ 5 The empirical formula of copper(I) oxide is Cu_2O . The percentages show that 88.8 g of copper combine with 11.2 g of oxygen, so

$$\text{amount of copper} = \frac{88.8 \text{ g}}{63.5 \text{ g mol}^{-1}} = 1.40 \text{ mol}$$

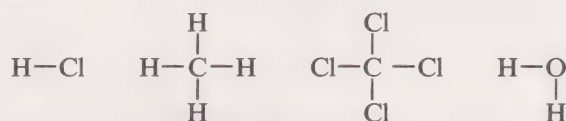
$$\text{amount of oxygen} = \frac{11.2 \text{ g}}{16.0 \text{ g mol}^{-1}} = 0.70 \text{ mol}$$

The ratio of the amounts of substance is

$$\frac{\text{copper}}{\text{oxygen}} = \frac{1.40}{0.70} = 2.0$$

Therefore the empirical formula is Cu_2O .

ITQ 6



The valencies are one for hydrogen and chlorine, two for oxygen and four for carbon. In each case, the number of lines issuing from an atom is equal to its valency.

SAQ ANSWERS AND COMMENTS

SAQ 1 Elements are always conserved in chemical reactions. Since hydrogen is present in one of the reactants, it must also be present in the products. When magnesium reacts with hydrogen chloride, hydrogen gas is also produced.

SAQ 2 The hydrogen in methane is not present in the product carbon dioxide. The reaction must therefore give an additional product, which does contain hydrogen. In fact it is water, a compound of hydrogen and oxygen.

SAQ 3 CuCl_2 .

3.00 g of Cu combine with 3.40 g of Cl. The amounts of combining substances are:

$$\text{amount of Cu} = \frac{3.00 \text{ g}}{63.5 \text{ g mol}^{-1}} = 4.72 \times 10^{-2} \text{ mol}$$

$$\text{amount of Cl} = \frac{3.40 \text{ g}}{35.5 \text{ g mol}^{-1}} = 9.58 \times 10^{-2} \text{ mol}$$

$$\frac{\text{amount of Cl}}{\text{amount of Cu}} = \frac{9.58 \times 10^{-2} \text{ mol}}{4.72 \times 10^{-2} \text{ mol}} = 2.03 \text{ (very nearly 2)}$$

The empirical formula is therefore CuCl_2 .

SAQ 4 Ag_2S .

8.70 g of Ag combine with 1.30 g of S. The amounts of combining elements are:

$$\text{amount of Ag} = \frac{8.70 \text{ g}}{108 \text{ g mol}^{-1}} = 8.06 \times 10^{-2} \text{ mol}$$

$$\text{amount of S} = \frac{1.30 \text{ g}}{32.1 \text{ g mol}^{-1}} = 4.05 \times 10^{-2} \text{ mol}$$

$$\frac{\text{amount of Ag}}{\text{amount of S}} = \frac{8.06 \times 10^{-2} \text{ mol}}{4.05 \times 10^{-2} \text{ mol}} = 1.99 \text{ (very nearly 2)}$$

The empirical formula is therefore Ag_2S .

SAQ 5 The empirical formula is HgO . From the data in the question, 4.63 g of mercury combine with 0.37 g of oxygen. The amounts of combining elements are:

$$\text{amount of Hg} = \frac{4.63 \text{ g}}{201 \text{ g mol}^{-1}} = 2.30 \times 10^{-2} \text{ mol}$$

$$\text{amount of O} = \frac{0.37 \text{ g}}{16.0 \text{ g mol}^{-1}} = 2.31 \times 10^{-2} \text{ mol}$$

$$\frac{\text{amount of Hg}}{\text{amount of O}} = \frac{2.30 \times 10^{-2} \text{ mol}}{2.31 \times 10^{-2} \text{ mol}} = 1.00$$

The empirical formula is therefore HgO .

SAQ 6 (i) According to Avogadro's law, the volumes can be represented by numbers of molecules. So we may write: 2 molecules of hydrogen plus 1 molecule of oxygen produce 2 molecules of water. Since each of the

molecules of water must contain at least one atom of oxygen, one molecule of oxygen contains at least two atoms.

(ii) Knowing that a molecule of hydrogen is H_2 , and assuming that oxygen is O_2 , we can say that a molecule of water has the formula H_2O .

(iii) $\text{H}_2(\text{g}); \text{O}_2(\text{g}); \text{H}_2\text{O}(\text{g})$.

SAQ 7 C_2H_2 .

A compound with the molecular formula CH would have a molar mass of about 13 g mol^{-1} (Appendix 1). The compound therefore has the molecular formula C_2H_2 .

SAQ 8 $\text{TiCl}_4 + 2\text{Mg} = \text{Ti} + 2\text{MgCl}_2$

To balance the equation, the ratio $\text{Mg}:\text{Cl}$ must be 1:2 as implied by the formula MgCl_2 . Therefore two atoms of Mg react with each unit of TiCl_4 .

SAQ 9 $\text{WO}_3 + 3\text{H}_2 = \text{W} + 3\text{H}_2\text{O}$

In water, H and O combine in the ratio 2:1. Therefore WO_3 reacts with the three molecules of H_2 to give three molecules of H_2O .

SAQ 10 $2\text{H}_2\text{S}(\text{g}) + \text{SO}_2(\text{g}) = 3\text{S}(\text{s}) + 2\text{H}_2\text{O}(\text{l})$

Again in water the ratio $\text{H}:\text{O}$ is 2:1. Therefore two molecules of H_2S react with one molecule of SO_2 .

SAQ 11 SiH_4 .

If the valency of silicon is four, one atom of silicon combines with four atoms of hydrogen.

SAQ 12 SO_3 .

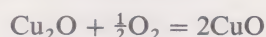
The valency of oxygen is two, so as the valency of sulphur is six, the ratio of sulphur atoms to oxygen atoms is 1:3.

SAQ 13 CO_2 and CCl_4 .

The valency of carbon in methane is equal to the number of hydrogen atoms that combine with one atom of carbon. It is four. Taking the valency of oxygen as two, we get the formula CO_2 by setting the valency of carbon equal to twice the number of oxygen atoms that combine with one atom of carbon.

SAQ 14 $2\text{Cu}_2\text{O} + \text{O}_2 = 4\text{CuO}$

The conversion of each Cu_2O into 2CuO requires one atom of oxygen. Oxygen occurs as molecules of formula O_2 , so we could write



However, we generally avoid writing fractions in chemical equations, in this case by multiplying by two.



SAQ 15 The valency of lead is two in PbO and four in PbO_2 . In each case the valency is equal to twice the number of oxygen atoms that combine with one atom of lead.

SAQ 16 X is aluminium and Y is tantalum. In the sixth Period of Figure 12, the Group V elements are tantalum (Ta) and bismuth (Bi). Of these, tantalum is in Group VA and bismuth is in Group VB.

SAQ 17 M could be hafnium or tin. As M forms only a single oxide, this must be its highest oxide. Elements with a highest oxide MO_2 , occur in Group IV of Mendeléeve's Table. This is apparent from trend 1 summarized at the end of Section 4.1. Of the elements (a)–(f), only hafnium and tin lie in Group IV. Note that as with carbon, silicon and titanium in your pack of data cards, the other Group IV elements also form a chloride MCl_4 . This is consistent with trend 3 of Section 4.1.

SAQ 18 Z is antimony (Sb). The *highest* oxide, Z_2O_5 , suggests a Group V element; trend 2, summarized at the end of Section 4.1, shows that Group V elements often form a hydride MH_3 . Figure 12 shows that the only Group V elements with relative atomic masses between 80 and 130 are niobium (Nb) and antimony (Sb). But Figure 13 shows that of these two, only antimony is a semi-metal.

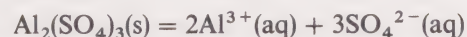
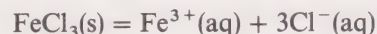
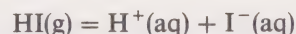
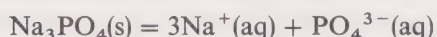
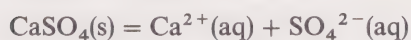
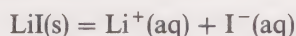
SAQ 19 Elements 16 and 28 have electronic configurations $1s^2 2s^2 2p^6 3s^2 3p^4$ and $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$, respectively. For revision on this, see Units 11–12 Section 9, and Section 5.1 in these Units. Element 16 has an outer electronic configuration $s^2 p^x$, and is therefore a typical element; element 28 has an outer electronic configuration $s^2 d^x$, which means that it is a transition element. Element 16 falls in Group VI of the Periodic Table: it is sulphur. Element 28 is nickel.

SAQ 20 M is vanadium. The highest oxide M_2O_5 suggests a Group V element in Mendeléeve's Table. The large number of fluorides with the formula type MF_n , in which the values of n differ by one, and the colourful nature of the compounds, suggest a transition element. Figures 12 and 17 show that the only Group V transition element with a relative atomic mass lower than 80 is vanadium. Its electronic configuration, derived from Figure 16, is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$.

SAQ 21 Element 110: $[\text{Rn}]7s^2 5f^{14} 6d^8$; element 114: $[\text{Rn}]7s^2 5f^{14} 6d^{10} 7p^2$; element 118: $[\text{Rn}]7s^2 5f^{14} 6d^{10} 7p^6$; element 119: $[\text{Rn}]7s^2 5f^{14} 6d^{10} 7p^6 8s^1$. Elements 110–120 have atoms with electronic configurations within the boundaries of Figure 16. After element 86, radon, where the 6p level is filled, the order of filling is 7s, 5f, 6d, 7p and 8s.

The answers to the final part of the question are (a) typical elements: 114, 118, 119; (b) transition element: 110; (c) alkali metal: 119; (d) noble gas: 118; (e) actinide: none. The different classes of element were defined in Sections 5.2 to 5.5.

SAQ 22



With the exception of FeCl_3 , the formulae and charges of the ions can be found in Table 5. Note that when the ions on the right-hand side of an equation are preceded by the correct numbers implied by the formulae of the solids on the left, the total charge on both sides is zero. Thus in $\text{Al}_2(\text{SO}_4)_3$, the subscript 2 against Al, and the subscript 3 against SO_4 tell us that two aluminium and three sulphate ions are formed. Obtaining the charges from Table 5 we get $2\text{Al}^{3+}(\text{aq}) + 3\text{SO}_4^{2-}(\text{aq})$ on the right-hand side, the total charge being $[(2 \times 3) + (3 \times -2)] = 0$. This requirement allows us to find the charge on the iron ion in the FeCl_3 equation. We know from Table 5 that chlorine forms $\text{Cl}^-(\text{aq})$, and the formula FeCl_3 tells us that three such ions must appear on the right-hand side. Because the total charge is zero, the single iron ion must have a charge of $+3$.

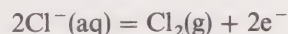
SAQ 23 Aluminium chloride, AlCl_3 ; magnesium sulphate, MgSO_4 ; ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$; calcium hydroxide, Ca(OH)_2 ; calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$.

You should use the names and Table 5 to deduce the ions that would be formed if the solids dissolved in water. Then you adjust the ratio of the ions to make the total charge zero and collect them together to get the formula of the solid compound. Thus calcium hydroxide will form calcium and hydroxide ions which, from Table 5 are Ca^{2+} and OH^- . Because the charges of ions that are formed add to zero, there must be two hydroxides for every calcium, so the formula is Ca(OH)_2 .

Note that where more than one *polyatomic* ion is collected up into the final formula, that ion is bracketed and the number set against it as a subscript. This is not necessary for monatomic ions. Thus in $\text{Ca}_3(\text{PO}_4)_2$, brackets are necessary around the polyatomic phosphate, but not around the monatomic calcium.

SAQ 24 (a) $\text{HCl(g)} = \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

The conductivity of the solution suggests that HCl dissolves to give ions, and from Table 5, the ions are H^+ and Cl^- .



If the hydrogen and chloride ions are discharged at the electrodes like the copper and chloride ions of CuCl_2 , then hydrogen gas should appear at the negative, and chlorine gas at the positive electrode. This is correct. From Section 3.1.1, you know that hydrogen and chlorine gases contain diatomic molecules. Thus as the equations imply, every pair of ions discharged gives a diatomic molecule.

SAQ 25 Strontium chloride and lithium phosphate are usually classified as ionic; ethanol and TNT as molecular covalent.

Both ionic substances have typically high melting temperatures and conduct electricity in the liquid state. Note that lithium phosphate has a very low solubility in water; so its conductivity in aqueous solution is not detectable; as noted in Section 6.4, this does not exclude its classification as an ionic substance.

Both molecular covalent substances dissolve in heptane, have low melting temperatures and are poor conductors in the liquid state. Although ethanol dissolves in water, its aqueous solution is a poor conductor and contains hardly any ions.

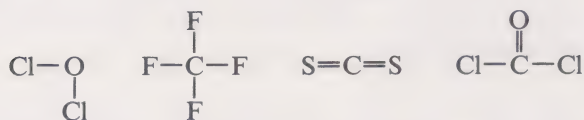
Note that in line with Section 6.7, the ionic substances are a combination of metallic elements from the left of Figure 17 with non-metallic elements from the right, the former appearing as monatomic cations (Li^+ , Sr^{2+}) and the latter as anions (PO_4^{3-} , Cl^-). The molecular covalent substances are combinations of non-metallic elements: carbon, nitrogen, hydrogen and oxygen.

SAQ 26 Of the ten substances, LiH , SrF_2 , LaBr_3 , TiO_2 and Al_2O_3 are the five leading candidates for the description 'ionic'; HF , SF_2 , PBr_3 , SO_2 and P_2O_3 are molecular covalent. You should have deduced this from point 4 of the summary that follows Section 6.7. Note however that TiO_2 and Al_2O_3 are here classified as ionic even though titanium, and especially aluminium, are not on the *extreme* left of the Periodic Table. Nevertheless, titanium and aluminium are both metals, unlike any element of which the five covalent substances are composed.

SAQ 27 The sulphide ion is S^{2-} : it has a charge of -2 . Potassium sulphide and magnesium sulphide are K_2S and MgS respectively. Sulphur atoms have six outer electrons ($3s^2 3p^4$), and can attain the noble gas configuration of argon by gaining two electrons. Potassium has one outer electron ($4s^1$) and magnesium has two ($3s^2$). By losing these, the atoms form the ions K^+ and Mg^{2+} , attaining the noble gas configurations of argon and neon, respectively. The compounds must be electrically neutral, so the ions combine in the ratios $(\text{K}^+)_2\text{S}^{2-}$ and $\text{Mg}^{2+}\text{S}^{2-}$.

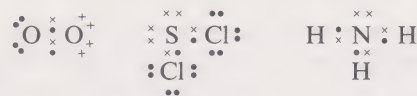
SAQ 28 The nitride ion is N^{3-} : it has a charge of -3 . Lithium and calcium nitrides are Li_3N and Ca_3N_2 respectively. Nitrogen has five outer electrons ($2s^2 2p^3$), and can gain the noble gas configuration of neon by gaining three electrons. Lithium and calcium have one and two outer electrons, respectively. By losing these, the atoms form the ions Li^+ and Ca^{2+} with the electronic configurations of helium and argon, respectively. The electrical neutrality of the compounds is ensured by combination in the ratios $(\text{Li}^+)_3\text{N}^{3-}$ and $(\text{Ca}^{2+})_3(\text{N}^{3-})_2$.

SAQ 29



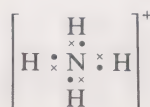
In each case, the number of lines issuing from each atom is equal to the atom's quoted valency.

SAQ 30 With six outer electrons each, the two oxygens in the O_2 molecule must form a double bond with each other if each is to attain a noble gas configuration. SCl_2 and NH_3 contain single bonds.

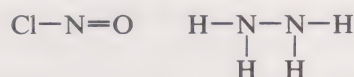


The O_2 molecule is thus $\text{O}=\text{O}$. In these structures, hydrogen attains the helium configuration, oxygen and nitrogen attain the neon configuration, and sulphur and chlorine the argon configuration.

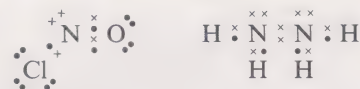
SAQ 31 Nitrogen has the outer electronic configuration $2s^2 2p^3$, so the N^+ ion has one electron less ($2s^2 2p^2$), which leaves four outer electrons. Combination with four hydrogen atoms to form the NH_4^+ ion then gives each atom a noble gas configuration:



SAQ 32 The only diagrams that give nitrogen a valency of three, oxygen a valency of two, and hydrogen and chlorine a valency of one are



These diagrams also lead to Lewis structures in which each atom gains a noble gas configuration with eight outer electrons.



SAQ 33 AlF_3 and SnF_4 are ionic substances; CF_4 and PF_3 are covalent. Phosphorus lies to the right of aluminium in the third Period of the Periodic Table, so it is more electronegative. The electronegativity of phosphorus is therefore closer to that of the very electronegative element fluorine. Thus the electronegativity difference between the elements is larger in AlF_3 than in PF_3 , and AlF_3 is more likely to be ionic. Likewise, tin lies below carbon in Group IV, and so is less electronegative: this time, the electronegativity difference is larger in SnF_4 than in CF_4 . A similar result is obtained by adapting the arguments in the summary of Section 6: the combination of two non-metals tends to yield covalent compounds, so CF_4 and PF_3 will be covalent. These conclusions are correct: for example, CF_4 and PF_3 are colourless gases at room temperature; AlF_3 and SnF_4 are colourless solids that do not melt below 700°C .

SAQ 34 (i) CaCl_2 ; (ii) IBr ; (iii) CaMg_2 .

The properties listed are characteristic of (i) an ionic substance, (ii) a covalent substance, and (iii) a metallic substance. CaCl_2 is a combination of elements from the extreme left and extreme right of the Periodic Table, so the electronegativity difference will be large and this will

be the ionic compound. IBr will be covalent because it is a combination of elements of high electronegativity from the extreme right of the Table. CaMg₂ will be a metallic alloy because it is a combination of metallic elements with low electronegativity from the left of the Table.

SAQ 35 Rb₂O is an ionic compound. This is apparent from its high melting temperature and structure in which each oxygen is surrounded by eight rubidiums and each rubidium by four oxygens. Such structures are characteristic of ionic compounds (Section 6.4).

CCl₄ and F₂O are covalent compounds. The low melting and boiling temperatures suggest discrete molecular compounds, and in the case of CCl₄, this is corroborated by the low conductivity of the liquid. For CCl₄ and F₂O, we can write the following Lewis structures



In the case of Rb₂O, the ions Rb⁺ and O²⁻ have noble gas configurations (krypton and neon, respectively). We can therefore write Rb₂O as (Rb⁺)₂O²⁻.

SAQ 36 The highest oxide H₂O and the formation of H⁺(aq) ions, together with the (outer) electronic configuration 1s¹, suggest a position in Group I above lithium.

However, since helium (1s²) is always placed above neon (1s²2s²2p⁶), electronic configuration seems less significant in the first Period, and the molecular gaseous nature of hydrogen, plus the formation of ionic hydrides, suggest a halogen-like position above fluorine. Also consistent with such a position are the formation of covalent compounds such as hydrogen halides and CH₄, in which hydrogen has a valency of one, and the fact that the highest oxide of fluorine is F₂O (see your pack of data cards). So there is a good case for putting hydrogen in Group VII above fluorine, especially as it is a non-metal, and non-metals appear on the right of the Periodic Table. A case for placing it in Group I above lithium exists, but it is perhaps somewhat weaker. It is because of the ambiguity that hydrogen is neither an alkali metal nor a halogen that it is left 'hanging in the air' in Figure 17.

SAQ 37 One litre of water contains 55.5 moles of water.

From Appendix 1, the molar mass of water is 18.02 g mol⁻¹. The number of moles of water in 1000 g is

$$\frac{1000 \text{ g}}{18.02 \text{ g mol}^{-1}} = 55.5 \text{ mol}$$

SAQ 38 A mole of copper is equivalent to the amount of copper in about 18 coins: one coin contains 3 × 10²² atoms. The molar mass of copper is 63.5 g mol⁻¹. The

number of coins in 1 mole is

$$\frac{63.5 \text{ g mol}^{-1}}{3.5 \text{ g}} \approx 18 \text{ mol}^{-1}$$

The number of moles in one coin is

$$\frac{\text{mass of coin}}{\text{molar mass of copper}} = \frac{3.5 \text{ g}}{63.5 \text{ g mol}^{-1}} = 0.055 \text{ mol}$$

The number of atoms in the coin is equal to number of moles multiplied by Avogadro's constant:

$$0.055 \text{ mol} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 3.3 \times 10^{22}$$

SAQ 39 A mole of nitrogen gas has a volume of 0.0230 m³. The molar mass of nitrogen (N₂) is 28.0 g mol⁻¹. From Units 5-6 you know that

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

Hence,

$$\begin{aligned} \text{volume of one mole} &= \frac{\text{mass of one mole}}{\text{density}} \\ &= \frac{28.0 \text{ g}}{1220 \text{ g m}^{-3}} = 0.0230 \text{ m}^3 \end{aligned}$$

This volume is equivalent to that in a cube with sides of approximately 28 cm.

SAQ 40 The empirical formula is PBr₅.

$$\begin{aligned} \text{number of moles of phosphorus atoms} &= \frac{1.00 \text{ g}}{31.0 \text{ g mol}^{-1}} \\ &= 0.0323 \text{ mol} \end{aligned}$$

Likewise, to find the number of moles of bromine atoms, we divide the mass of combined bromine by the molar mass:

$$\begin{aligned} \text{number of moles of bromine atoms} &= \frac{12.90 \text{ g}}{79.9 \text{ g mol}^{-1}} \\ &= 0.161 \text{ mol} \end{aligned}$$

Notice that the relative atomic mass of bromine is half the molar mass of the Br₂ molecules in the bromine that reacts.

$$\text{relative numbers of moles } \frac{\text{Br}}{\text{P}} = \frac{0.161}{0.0323} = 4.98$$

This ratio is not significantly different from 5.

SAQ 41 SbBr₃.

Since some antimony remains unchanged, it was used in excess. You need to calculate the number of moles of each reactant consumed.

$$\begin{aligned} \text{amount of Sb} &= \frac{(5.00 - 2.46) \text{ g}}{122 \text{ g mol}^{-1}} \\ &= 0.0208 \text{ mol of Sb atoms} \end{aligned}$$

$$\begin{aligned} \text{amount of Br} &= \frac{5 \text{ g}}{79.9 \text{ g mol}^{-1}} \\ &= 0.0626 \text{ mol of Br atoms} \end{aligned}$$

The ratio gives the empirical formula:

$$\frac{\text{Br}}{\text{Sb}} = \frac{0.0626 \text{ mol}}{0.0208 \text{ mol}} = 3.01$$

This ratio of Br atoms to Sb atoms is not significantly different from 3. The formula is therefore SbBr_3 .

SAQ 42 SF_6 .

If 1.00 g of sulphur gives 4.56 g of product, the product contains 3.56 g of fluorine. First determine the number of moles.

$$\begin{aligned} \text{amount of sulphur} &= \frac{1.00 \text{ g}}{32.1 \text{ g mol}^{-1}} \\ &= 0.0312 \text{ mol of S atoms} \end{aligned}$$

$$\begin{aligned} \text{amount of fluorine} &= \frac{3.56 \text{ g}}{19.0 \text{ g mol}^{-1}} \\ &= 0.187 \text{ mol of F atoms} \end{aligned}$$

$$\text{the mole ratio } \frac{\text{F}}{\text{S}} = \frac{0.187 \text{ mol}}{0.0312 \text{ mol}} = 5.99$$

This ratio is not significantly different from 6. The formula is therefore SF_6 .

SAQ 43 The valencies are five (P), three (Sb) and six (S).

From the formula PBr_5 , you can see that one atom of phosphorus combines with five atoms of bromine. In SbBr_3 , one atom of antimony combines with three atoms of bromine. In SF_6 , one atom of sulphur combines with six atoms of fluorine.

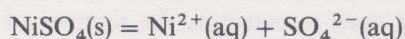
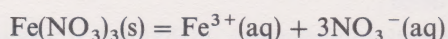
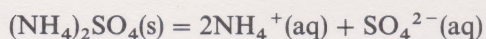
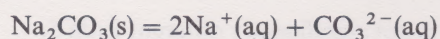
SAQ 44 The valency of iron in Fe_2O_3 is three.

In Fe_2O_3 , iron atoms combine with oxygen atoms in the ratio 2:3. Remember, if y atoms of A combine with x atoms of B, then the valencies of A and B are in the ratio $x:y$. Thus the valencies of iron and oxygen are in the ratio 3:2. Because the valency of oxygen is two, that of iron is three.

SAQ 45 Ag_2O .

The ratio of the valencies of silver and oxygen is 1:2, so the atoms combine in the ratio 2:1.

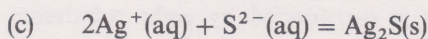
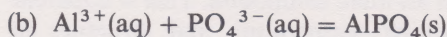
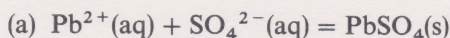
SAQ 46



The ions in the first two equations are all listed in Table 5. Notice that the ions are written showing the correct number that are formed from the formula on the left-hand side of the equation. This is necessary to ensure that the equation is balanced. You can infer from the formula $\text{Fe}(\text{NO}_3)_3$ that the ion $\text{Fe}^{3+}(\text{aq})$ is formed because three ions $\text{NO}_3^-(\text{aq})$ are also formed. The total charge on the left is zero, and so it must also be zero on the right. Thus three NO_3^- ions have a total charge of

−3, and so the charge of Fe must be +3. Similarly, nickel is an element not listed in Table 5. As NiSO_4 has zero charge, the nickel ion must have the opposite charge of SO_4^{2-} . It is Ni^{2+} .

SAQ 47



In each case, the ratio of ions that react is written to ensure that the net charge (zero) is the same on each side of the equation.

SAQ 48 $2\text{P}(\text{s}) + 5\text{Br}_2(\text{l}) = 2\text{PBr}_5(\text{s})$

The ratio 1:5 for the atoms P and Br in the product requires the same ratio in the reactants. To avoid writing fractions, such as $2\frac{1}{2}\text{Br}_2$, we take 5Br_2 with 2P .

SAQ 49 $\text{S}(\text{s}) + 3\text{F}_2(\text{g}) = \text{SF}_6(\text{g})$

Fluorine is represented by F_2 , and so three molecules of F_2 combine with one atom of sulphur.

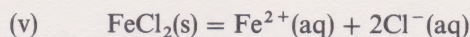
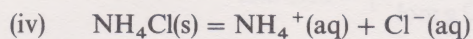
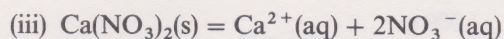
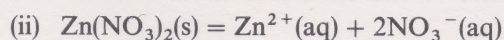
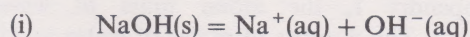
SAQ 50 $2\text{C}_4\text{H}_{10} + 13\text{O}_2 = 8\text{CO}_2 + 10\text{H}_2\text{O}$

In this example, the balancing is most easily done by leaving oxygen until last. One molecule of C_4H_{10} would burn to yield four molecules of CO_2 (accounting for the four carbon atoms) and five molecules of H_2O (accounting for ten hydrogen atoms). These products, however, require a number of oxygen molecules ($6\frac{1}{2}$) that is not a whole number. So the reaction is written with *two* molecules of C_4H_{10} . Thus 13 molecules of O_2 are required to balance the equation.

SAQ 51 $\text{PCl}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HCl}$

You should begin by selecting a product that will help you to establish the ratio of the reactant molecules. Since hydrogen is present in both products, it is probably more sensible to choose H_3PO_3 , in which the PO_3 grouping establishes the ratio of P:O as 1:3. Therefore, take one molecule of PCl_3 and three molecules of H_2O , giving a ratio of 1:3 for P:O in reactants. The presence of three chlorine atoms in PCl_3 requires three molecules of HCl to balance the chlorine. If you check the last element, hydrogen, you now find six atoms on each side; the equation balances.

SAQ 52 The following equations show which ions are produced. Remember that some ions are complex ions that do not usually dissociate in water (Table 5), and remember too that all charges must balance. This helps you to determine the charge of unfamiliar ions.



Notice that for examples (ii), (iii) and (v) we have not written $(\text{NO}_3)_2^-$ or Cl_2^- . For example, 2Cl^- means

two separate chloride ions, Cl^- , whereas Cl_2^- means a molecule of chlorine, Cl_2 , having one negative charge.

SAQ 53 According to Figures 15 and 16, element 34 has the electronic structure $[\text{Ar}]4s^23d^{10}4p^4$, and is in Group VI of the Periodic Table. Element 38 has the electronic structure $[\text{Kr}]5s^2$, and is in Group II of the Periodic Table.

These elements are selenium and strontium, and the highest oxides are expected to have the formulae SeO_3 and SrO . The highest hydrides should be SeH_2 and SrH_2 . The binary compound formed between Se and Sr would be SrSe , corresponding to the ionic formulation $\text{Sr}^{2+}\text{Se}^{2-}$, in which strontium and selenium both attain the electronic configuration of the noble gas krypton.

SAQ 54 The element Se lies on the right-hand side of the Periodic Table in Figure 17 and, like hydrogen and oxygen, is a non-metal. The element Sr lies on the left-hand side of the Periodic Table and is a metal. Thus, SrO , SrSe and SrH_2 are expected to be ionic compounds, and SeH_2 and SeO_3 are expected to be covalent compounds.

SAQ 55 (i) Element X most likely lies in Group V of Mendelée's Table (Figure 12). From the formulae of the hydride and chloride, X would be placed in Groups III or V. The properties of the chloride XCl_3 suggest that the compound is covalent, and this is consistent with the conductivity of the solid element, which implies that X is a non-metal or semi-metal. So we conclude that X is placed in Group VB of Mendelée's Table. Thus X is one of the elements N, P, As or Sb. It is not Bi because this is a metal. (In fact X is arsenic.) X is therefore a typical element and has an outer electronic configuration of the type s^2p^3 .

(ii) The variety of valencies of Y in its oxides and the colours of these compounds tell us that Y is a transition element. If Y_2O_7 is the highest oxide of Y, it is therefore

one of the metals in Group VIIA of Mendelée's Table. Its outer electronic configuration is therefore $ns^2(n-1)d^5$, and it is one of the elements Mn, Tc or Re.

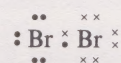
SAQ 56 From Table 5, you can obtain the charge on the cations in these compounds: Mg^{2+} and Al^{3+} . Phosphorus is a typical element in Group V of the Periodic Table (Figure 17) and the atom is required to gain three electrons to have the electronic configuration of the noble gas argon. The phosphide anion is therefore P^{3-} .

The formula of the compounds formed from these ions are obtained from the number of ions that combine to give neutral compounds. These formulae are Mg_3P_2 and AlP .

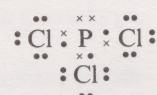
SAQ 57 Selenium is in Group VI of the Periodic Table and has six outer electrons (s^2p^4). It attains a noble gas configuration by sharing two electrons with each hydrogen atom and is represented by this structure:



Bromine has seven outer electrons (s^2p^5). It attains a noble gas configuration by forming a single bond between two atoms:



Phosphorus has five outer electrons (s^2p^3). In its covalent compounds it attains the electronic configuration of a noble gas by forming three covalent bonds. Chlorine (s^2p^5) forms one covalent bond to gain the noble gas configuration. So PCl_3 is represented as



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